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November

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Name .... Title.................

Company ....

Street ....

City and Zone .... State...............

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Journal of METALS

Published to provide a continuing, authoritative, and up-to-date record of technologic, engineering, and economic progress in all branches of the metals industry by the

Metals Branch
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The AIME Publishes:
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VOL. 188, NO. 11 NOVEMBER, 1950

IN TWO SECTIONS—SECTION I

COVER

A production record was established when Firestone Tire & Rubber Co., in 30 days, delivered 300 57-mm recoilless rifles needed in Korea. Here, U. S. Army Ordnance inspectors are shown on the final inspection operation. A dummy shell is inserted to check for specified firing-pin protrusion and mechanical extraction of empty case, and a star gauge measures the lands and grooves of the rifling inside the barrel. A borescope is used to check the inside of the barrel for defects.

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Authors In This Issue

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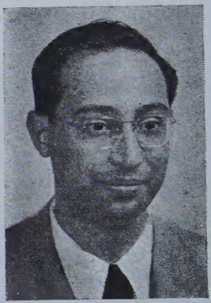
D. F. Clifton (p. 1329), Engineering Experiment Station Fellow at the University of Utah, was formerly Metallurgist at Globe Steel Tube Co., Milwaukee, and the Institute for the Study of Metals, University of Chicago. He received his B.S. in Met. E. degree from Michigan College of Mining and Technology, and enjoys sailing, hiking, and books.



L. D. Jaffe

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J. B. Seabrook (p. 1317). See JOURNAL OF METALS, December, 1949.

N. J. Grant (p. 1317). See JOURNAL OF METALS, October, 1950.

Dennis Carney (p. 1317). See JOURNAL OF METALS, February, 1950.

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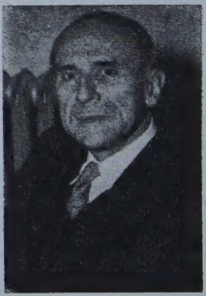
M. E. Fine (p. 1322). See JOURNAL OF METALS, July, 1950.

C. S. Barrett (p. 1329). See JOURNAL OF METALS, September, 1949.



W. J. Kroll

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R. K. Pitler

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*Zinc, lead, and other metals are being recovered commercially from slag piles at three plants now in operation. Designed by Babcock & Wilcox Co., these plants recover the metals by slag fuming or remelting the slags and collecting the fumes. These vapors are converted into metallic oxides, and then collected as solids or powders.

*British Aluminium Co., Ltd. and Aluminium, Ltd., Montreal, Canada, are planning a joint study of the suitability of sites in British North Borneo and the Gold Coast for aluminum reduction plants.

*For measuring ductility of brittle metals, a method has been developed whereby the metal is bent over an especially formed bar in which the radius of curvature decreases progressively. Radii at each point are predetermined, and elongation is read from a graph of radius of curvature at the point of fracture vs known bar thickness. The scale and proportions are arbitrary and are selected to accommodate specific ranges.

*Complete dependence on foreign sources for cobalt will end when Calera Mining Co., at Forney, Idaho, gets its mine and mill into production. Yield is estimated to total about 2 million lb of metallic cobalt per year.

*Electrical and industrial companies of Netherlands have joined in raising funds to erect an uranium pile at Arnhem for testing electrical materials; and later for studying atomic fission, using the generated heat for producing electricity.

*Contracts have been awarded, totalling $35 million, for aircraft rocket assembly and loading facilities at the Naval Ordnance Depot, Shumaker, Ark.

*Bituminous Coal Institute estimates that completely mechanized heating and boiler plants will save 25 pct of the cost of operating a hand-fired plant. Coal consumption is reduced, and labor savings are substantial.

*A saving of $5000 a year in Navy Bureau of Aeronautics electroplating shops has been effected by using technical grade hydrogen peroxide instead of chemically pure grade.

*A method of forging aircraft wing panels has been developed, according to the Air Materiel Command. Wing skins are forged integrally with stiffeners or bracing, making strengthening unnecessary. Material and labor costs are reduced substantially, but perhaps more important is elimination of the need for the vast number of high cost and critically short special machine tools.

*By the substitution of titanium for steel in the base plate and redesigning, the 81 mm mortar was reduced in weight by about 50 pct. Ordnance is currently designing prototypes of a considerable number of items of equipment utilizing titanium, as well as new designes, in order to improve the equipment and cut down its weight.

*A loan, perhaps as great as $100 million, from American insurance companies is about negotiated for development of Labrador iron ore properties. The program will call for a total expenditure of up to $200 million, including, as well as all mine development work, the power facilities, housing for mining personnel, and auxiliary equipment.

The Drift of Things

. . . . as followed by Edward H. Robie

The New Directory

Provided no cataclysmic acts of God or man intervene, which is by no means unlikely, the 1950 Directory of AIME members should be mailed with this issue of the journals. Its publication has caused more grief to the Institute's secretarial staff than anything that has happened in the last two years. One of the secretaries of the other national engineering societies suggested the other day that we all get together and compare notes as to the best method of publishing a Directory, inasmuch as it seemed to be a problem for everybody. We offered to contribute a well documented memorandum on how *not* to publish one.

The 1948 Directory—the last one issued—was published in June of that year. It followed the style of previous volumes, and it cost a little more than $14,000. This year we aimed to get out a more accurate Directory at materially less cost. To make it more accurate we decided not to print it from our master file cards of members' names, positions, and addresses, since many had changed their positions without notifying us. So last March we sent a reply postal card to every member asking for his name, grade of membership, year of election, title, name of employer, address, and whether or not available for consulting work. This, we fondly thought, would give us an up-to-the-minute record of our membership, which, with a little editing, we could send to the printer. But, after waiting two months, some 5,000 of our members had not returned the card. So we had to make one out for them, from our admittedly not entirely up-to-date records.

As a further improvement in the Directory we decided to incorporate a company listing in the geographical section. That is, every company employing a member would be listed under the respective states and countries, with the names of the members, and their positions, listed in each town. This was intended to be a great convenience to members. We had the directory of the Society of Automotive Engineers as a model in this respect. It was a pious idea, with some devilish pitfalls.

As we have said, reduction of cost was one of our aims, and we thought we could eliminate about one third of the former cost. We decided to omit much of the first 115 pages of the former Directory—that part devoted to medals and awards, bylaws, the annual reports, etc., which would be printed, say, every five years. Also to be omitted were some forty pages devoted to Student Associates, since a large proportion of these addresses become obsolete at the end of a school year. A considerable further saving was expected by having the Directory set up on IBM electric typewriters and printed by offset. Another economy considered was the idea of sending a Directory only to those who request it. This is the practice followed by the AIEE for instance, and of their 37,000 members less than 5000 ask to have a directory. This would mean a substantial saving but we felt that all AIME members had always received our Directory and would expect one without asking for it; also that even though they might not want one now they would find it useful at certain times in the future and then would not have it, necessitating more correspondence with AIME headquarters.

Some of the reasons for delay in publication and for increases over expected costs have been indicated. There were many others. We first planned to issue the book in the spring. Then by May we hoped to have it out by Sept. 1. As we write this it is Oct. 17 and we have not seen a copy yet. As the days went by, printing and binding costs increased. The ultimate cost promises to be a little more than that for the 1948 volume.

We shall be glad to have your comments for our future guidance. The book has many good points which we shall try to continue in future editions. Its faults we shall try to avoid.

Mexico City, Oct. 28-Nov. 3, 1951

Dates have now been definitely set for the AIME Regional Meeting next year in Mexico City—Oct. 28 to Nov. 3. As already announced, the meeting will be held jointly with the Instituto Nacional para la Investigacion de Recursos Minerales, and if you can't pronounce that, or don't know what it means, then it is not too early to begin to do something about it. You will get along O.K. and have a good time in Mexico City next October if you don't know a word of Spanish, but you'll have a better time if you know a bit about how they talk south of the border.

In the week before the meeting the American Mining Congress will gather at Los Angeles—Oct. 22-24—leaving three or four days to go from there to the capital of Mexico. Originally our meeting was tentatively scheduled for Oct. 15-20, but the American Society for Metals has now shifted its Detroit meeting to that week, and every effort is being made to avoid conflicts.

We are assured that the end of October is an ideal time to visit Mexico. The rainy season will have ended and the weather will be just right. Attractive trips will be arranged to such places as Taxco, Xochimilco, the Pyramids, San José de Purula, and to the old mining camp of Pachuca, still active. Even Paracutin, the new volcano, may be in eruption and worth a visit.

You can save enough money on Christmas presents alone to pay a good share of the expenses of the trip. Table silver, belt buckles, cuff links, tie pins, cigarette cases, compacts, perfume, carved wood, tooled leather, gold jewelry, blankets, serapes, glazed pottery are all good buys. Each person can bring back $200 worth, or $500 worth if they stay more than twelve days. See the September issue of Esquire as to how economical this vacation trip can be.

Just enough technical sessions to justify the trip, if you are on an expense account.

Muddled Geography

From the Baker Hotel in Dallas comes a letter which asks if we will not consider that city for a forthcoming meeting of the New England Conference of the Institute of Metals Division of the Institute. Heretofore this conference has been held in such places as Boston, Springfield, Providence, and New Haven. Doubtless Dallas offers attractions not heretofore enjoyed. How about the Petroleum Branch coming up to Boston for one of their fall meetings? Though the continental shelf along the Gulf Coast has been found to contain oil, the same shelf off New England has not yet been investigated for anything but fish.

And another convention bid: "We have just learned that your organization is planning a convention in Chicago, during the month of Chicago."

Electric Furnace Steel Men to Meet

Production, quality, and economy, will be the basic theme of the 8th Annual Electric Furnace Steel Conference, Dec. 7, 8 and 9. This conference will bring together the top operating, maintenance, metallurgical, refractory, control, and electrical personnel of practically all of the steel mills and foundries producing electric furnace steel. The three-day meeting will be held at the William Penn Hotel, Pittsburgh, Pa.

Advance registration is urged to avoid confusion and congestion at the meeting. Past registrants will receive application blanks by mail. Application blanks also may be obtained from Ernest Kirkendall, Room 905, 29 West 39th St., New York 18, N. Y. Everyone attending must register.

The registration fee of $7.00 to nonmembers and $5.00 to members of AIME includes admission to all sessions, a bound copy of the Proceedings to be published later, and the Journal of Metals Electric Furnace Conference Special Program Issue. Students and those attending only the Educational Session will not be required to register unless the Proceedings volume is desired.

Discussion of all topics is invited. Oral discussion will be limited to 5 min., and longer discussions summarized orally, with the complete written discussion submitted for publication in the Proceedings.

Dinner tickets, which will also admit the holder to the cocktail party, should be purchased in advance. Individual tickets are $7.50 (including gratuities). Reserved and placarded tables of 10 may be obtained for $85, by contacting Bedell Baxter, Basic Refractories Inc., Farmers Bldg., Pittsburgh, Pa.

Hotel reservations should be made directly with the headquarters hotel or other Pittsburgh hotels.

Electric Furnace Conference

JOURNAL OF METALS will spotlight the Electric Furnace Steel Conference with a special issue in December. The Electric Furnace Conference Special Issue will carry a detailed program of each meeting, showing the title of papers, speakers, sessions, meeting times and places, and all general activities such as plant trips, luncheons, etc. Some of the papers to be presented at the Conference will be featured, and the entire issue will be designed around the conference.

Electric Furnace Steel Sessions

Acid and Basic Session

General Session

Chairman's Welcoming Remarks; Announcements and Reports.

Raw Materials

Use of Iron Ore in Steelmaking; Scrap-Availability, Present Physical Condition, Contamination; Slag Material and Slag Action in Basic Arc Furnace.

Educational Session

Effect of Residuals and Their Removal; Motion Pictures on Controlled Production of Alloy Steels; Question Period—Panel of Experts.

The Educational Session is planned to be especially helpful to melters, helpers, observers, young metallurgists and students. It has proved to be a very valuable refresher course to the regular registrants at the Conference.

Acid Sessions

Oxidation Practice (Boil)

Ore Practice; Oxygen Practice.

Experience With Special Deoxidizers

New Special Deoxidizers; Effect of Various Deoxidation Treatments Upon Type of Inclusion and Properties of Cast Steels; High Silicon Steels; Carbortam as a Deoxidizer.

Temperature Control

Production Control of Molten Steel Temperature and its Effect on Steel Casting Quality.

Basic Sessions

Continuous Casting

Mold Design; Casting Shape; Melting Practice and Refractories; Control of Process; Quality and Products; Typical Production Layouts.

Furnace Maintenance and Rebuilding

Bottom Building and Maintenance; Top Charging and High Voltages in Lining Life and Repair; Types of Roof Construction; Relining Time; Materials Used and Specifications; Applications of a Resistance Indicator.

Melting Practice

Metallurgy; Tool Steels; Simple and Carbon Steels; Rimming and Carbon Steels; Induction Melting; Stainless Steels.

Investigation of New Special Deoxidizers

by C. G. Mickelson

THE ultimate goal in the steel casting industry is to produce a product which will have the most desirable physical properties and be sound and free from pinhole porosity and other known defects. At the present time the use of aluminum in most grades of cast steel is necessary to completely eliminate any difficulties which might result from pinhole porosity. There are, of course, exceptions to this rule and certain grades of steel or certain types of castings can possibly be produced without the use of aluminum. There are times that when only aluminum is added certain physical properties are not as satisfactory as when other additions are used with the aluminum or in place of it.

In an investigation of numerous types of deoxidizers it has been found that some produce excellent results while others are of little value. This paper will merely touch on four of these special additions.

When aluminum was used as a deoxidizing agent it was observed that certain heats did not have the best ductility properties desired for specific types of products. The use of the proper amount of aluminum resulted in the formation of crystalline or Type 3 inclusions which produced satisfactory physical properties for certain grades of steel. The high tensile steel requiring 60,000 psi yield, 90,000 psi tensile, 22 pct elongation and 45 pct reduction of area is one of these grades. For certain specifications the yield and tensile properties remain the same but the elongation and reduction of area are increased to 25 and 50 pct, respectively. For such specifications low ductilities are occasionally experienced on a definite percentage of the heats. This condition is considerably aggravated and more pronounced in acid practice where the sulphur contents are somewhat higher. It is known from past experiences that the round type of inclusions are the most desirable for obtaining high ductility properties. Considerable information has been presented by a number of investigators, especially by Mr. A. P. Gagnebine,[1] regarding the use of selenium. This element might well be used for obtaining the desired round inclusions and the desired high physical properties. In some previous work it was observed that selenium used alone would not eliminate pinhole porosity on normal grades of steel as determined by our porosity test casting and X-ray examination. The porosity test casting consists of a flat plate approximately ⅞ in. in thickness, 6 in. wide and 7 in. long. It is gated in one corner, with a pop riser located on the opposite corner. Because selenium does not eliminate pinhole porosity it was decided to use this element in conjunction with varying amounts of aluminum. The aluminum was added to control the porosity while the selenium was used to control the type of inclusions. In the initial laboratory investigations, split heats were produced in the induction furnace with varying aluminum additions made to the first part of the heat and varying amounts of aluminum and selenium added to the second part of the heat. Table I illustrates the average results which were obtained after standard heat treatment. It can be noted that the ductility properties improved when the proper amount of selenium was added to the steel. In the metallographic investigation it was found that when the proper addition of selenium was added to the steel containing either ½ lb or 2 lb of aluminum per ton of charge the inclusions were changed from the elongated or crystalline type to the round type.

Table I—Comparison of Physical Properties of High Tensile Steel With and Without the Selenium Addition

Heat	Deoxidizer Per Ton	Yield, Psi	Tensile, Psi	Elong., Pct	Red. Area Pct
1	0.5 lb Al	65,100	93,000	25.5	42.6
	+0.05 pct Se	69,900	94,100	27.6	50.3
2	0.5 lb Al	65,400	90,600	25.6	39.4
	+0.15 pct Se	64,500	88,400	29.2	53.9
3	0.5 lb Al	72,800	95,700	25.3	41.3
	+0.30 pct Se	68,400	90,300	27.9	48.8
4	0.5 lb Al	65,600	91,300	26.3	43.3
	+0.50 pct Se	64,200	87,400	27.0	48.7
5	2 lb Al	64,600	91,100	27.8	49.3
	+0.05 pct Se	67,200	91,800	27.8	46.8
6	2 lb Al	67,100	95,300	27.0	50.8
	+0.15 pct Se	67,000	94,100	28.0	51.9
7	2 lb Al	66,000	94,800	26.8	50.9
	+0.30 pct Se	64,700	90,200	28.8	52.2
8	2 lb Al	65,000	92,100	28.6	53.5
	+0.50 pct Se	64,600	90,000	29.2	52.2

Additional experiments were made, using 1½ lb of aluminum with selenium additions varying between 0.075 pct and 0.10 pct. In these heats excellent results were obtained. The average physical properties ranged approximately 66,000 psi yield, 101,000 psi tensile, 26 pct elongation and 54 pct reduction of area.

With these promising results, experiments were tried in the acid electric shops and satisfactory ductility properties were obtained. The ductility results were considerably above those normally obtained on a similar grade of steel treated only with aluminum.

It was noted in one of the shops that when the scrap from these selenium heats was kept segregated and used over and over again with additional selenium added, a buildup of selenium resulted. This buildup of selenium seemed to reduce the fluidity properties of the steel. However,

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if the selenium addition would be added to only a few heats per day and the scrap from these heats would not be segregated, no difficulties regarding pouring would be encountered. At one of the shops this addition of selenium is now being used as standard practice in the production of premium types of work. The high cost prohibits its use on all heats but it can economically be used on special specification work.

Graphidox

In the high tensile steel, which requires meeting 60,000 psi yield, 90,000 psi tensile, 22 pct elongation and 45 pct reduction of area, some difficulty was encountered when a change was made from the practice of using 5 lb of high carbon ferrotitanium per ton of charge to the practice of using 2½ lb of aluminum per ton of charge. This change was made in order to improve the general practice and produce castings completely free of pinhole porosity. Satisfactory results were obtained under laboratory conditions but from time to time in the shop certain difficulties occurred. One difficulty was that on a certain percentage of the heats lower reduction of area properties were obtained than when titanium was used. This lower reduction of area was due to the presence of some elongated inclusions. In addition it was found that a more rapid cooling from the molten state was conducive to the formation of elongated inclusions. This was observed where either chilled molds were used or where very light sections were poured.

Another problem encountered was the lower yield point obtained with the aluminum treated steel. This was especially critical when bars were attached to castings and cooled in large heat treating furnace loads.

Table II—Comparison of Physical Properties from Split Heats Deoxidized with Aluminum and Aluminum Plus Graphidox

Heat	Deoxidizer Per Ton, Lb	Temp., °F	Yield, Psi	Tensile, Psi	Elong., Pct	Red. Area, Pct	Charpy, Ft-Lb
1	Al—2½	950	66,400	96,700	26.4	52.1	50.6
		1050	64,100	95,700	26.6	50.9	49.4
	Al—2½ Graphidox-3	950	70,000	100,200	26.5	52.2	47.8
		1050	69,100	99,000	26.4	50.9	49.4
2	Al—1¼	950	69,100	102,200	24.9	50.1	48.9
		1050	68,200	100,500	26.0	53.2	46.0
	Al—1¼ Graphidox-3	950	73,300	104,200	24.0	48.6	46.0
		1050	73,100	102,900	25.6	50.5	42.2
3	Al—⅝	950	68,100	101,600	22.0	38.1	33.4
		1050	67,000	100,100	21.2	38.4	31.3
	Al—⅝ Graphidox-3	950	73,600	104,800	25.4	52.2	46.5
		1050	72,600	102,900	25.4	50.7	42.0

In an effort to correct these two conditions, research investigations were conducted using two different materials—one called Graphidox and the other calcium-manganese-silicon. Most people are familiar with the calcium-manganese-silicon alloy addition as a number of papers have been presented on this subject. Graphidox is an alloy containing 6 pct calcium, 50 pct silicon and 10 pct titanium. Again split heats were produced using the regular aluminum addition of 2½ lb per ton. Other heats were made with smaller additions of aluminum so as to vary the types of inclusions obtained. In the second half of the aluminum treated heats, 3 lb of Graphidox or 3 lb of calcium-manganese-silicon was used in addition to the aluminum. The general analyses of the steel used in this investigation contained 0.31 pct carbon, 1.65 pct manganese, 45 pct silicon, 0.015 pct phosphorus and 0.035 pct sulphur. Average results of this work can be seen in Tables II and III. It is interesting to note that the average increase in the yield point was approximately 4800 psi when Graphidox was added to the aluminum treated steel and only 500 psi when calcium-manganese-silicon was added to a similar aluminum treated steel. In other words, the Graphidox addition definitely helped to improve the low yield properties which were causing plant troubles.

Table III—Comparison of Physical Properties from Split Heats Deoxidized with Aluminum and Aluminum Plus Ca-Mn-Si

Heat	Deoxidizer Per Ton, Lb	Temp., °F	Yield, Psi	Tensile, Psi	Elong., Pct	Red. Area, Pct	Charpy, Ft-Lb
4	Al—2½	950	68,900	102,700	24.4	49.7	44.3
		1050	67,900	100,100	25.1	51.3	43.3
	Al—2½ Ca-Mn-Si -3	950	71,200	105,500	25.2	52.9	44.3
		1050	67,300	103,000	25.4	51.5	43.1
5	Al--1¼	950	66,300	94,400	26.4	52.2	47.9
		1050	63,300	91,400	27.4	51.7	49.0
	Al—1¼ Ca-Mn-Si -3	950	66,500	96,700	27.7	56.9	62.7
		1050	64,100	93,700	28.8	57.2	60.0
6	Al—⅝	950	71,100	104,900	20.4	39.5	34.5
		1050	70,900	101,800	21.4	39.4	32.2
	Al—⅝ Ca-Mn-Si -3	950	70,600	105,300	24.9	52.0	44.4
		1050	69,500	101,800	25.1	52.0	43.4

Both special additions improved the inclusions and physical properties of the steels containing ⅝ lb of aluminum per ton. When this amount of aluminum was added elongated inclusions were obtained; however, when Graphidox or calcium-manganese-silicon was added the elongated inclusions were transformed to the crystalline type. Further work on this subject was performed, showing that the Graphidox addition could be added either before or after the ⅝ lb of aluminum addition and still change the elongated inclusions to the crystalline type. Results of this comparison can be seen in Table IV.

Plant experiments indicated similar and encouraging results under production conditions.

Silicon-Magnesium-Aluminum

It has always been found desirable to stock as few items as possible and to make only the minimum number of additions to the molten steel. It is believed that the minimum number of additions made to the molten metal will not only produce a better grade of steel but will produce it at a reduction in cost.

An alloy containing approximately 40 pct silicon, 7.5 pct magnesium and 3.5 pct aluminum was submitted for consideration as an addition which could replace the 50 pct ferrosilicon, the aluminum and the calcium-manganese-silicon additions. If this material could be used it would be necessary to stock only one item instead of three, to weigh only one material, and to make only one addition to the molten metal. To invesigate this material, grade B and high tensile steels were produced in the laboratory induction furnace. The grade B steel analyzed about 0.26 pct

Table IV—Comparison of Physical Properties of High Tensile Steel Treated with Graphidox

Heat	Yield, Psi	Tensile, Psi	Elong., Pct	Red. Area, Pct	Charpy, Ft-Lb
A	73,700	104,500	25.0	52.6	45.5
B	72,600	103,900	25.6	52.5	47.3

A—Graphidox before aluminum, B—Graphidox after Aluminum carbon, 0.70 pct manganese, 0.45 pct silicon, 0.015 pct phosphorus and 0.035 pct sulphur. The high tensile heats averaged about 0.31 pct carbon and 1.65 pct manganese with the other elements being the same as grade B. All heats were melted in a similar manner except that the residual silicons in both grades of steels were varied from 0.01 to 0.40 pct. This variation in the residual silicon content allowed for deviations in the special alloy additions.

In a basic melting practice normally a 0.01 pct residual silicon would be obtained. However, in an acid melting practice the residuals in silicon could vary up to 0.40 pct, depending upon the temperature at which the metal was tapped from the furnace. A high residual silicon would necessitate the use of less special alloy, which in turn would lower the amount of aluminum and magnesium added. A condition like this would cause difficulties both in porosity and in inclusions. The steel from the heats produced was poured into standard test block molds and porosity test plates. Fig. 1 illustrates the condition of the porosity test plate when properly deoxidized with aluminum. Note the complete absence of pinhole porosity. Fig. 2 represents a similar plate, except that in this case only silicon was used as a deoxidizer. Note the extreme amount of porosity that can be obtained in this test casting. It has been found that the amount of porosity in this plate will depend upon the type of steel, the strength and quantity of the deoxidizer used.

It was observed on both grades of steel in this experiment that the special deoxidizer completely eliminated pinhole porosity when the residual silicon was 0.10 pct or less. In both grades of steel when the residual silicon was 0.20 pct a slight amount of porosity was observed in the test plates. When the residual silicons were increased to 0.30 and 0.40 pct considerable porosity was observed. There was no doubt that insufficient aluminum and magnesium were added to completely deoxidize the steel when the silicon residuals were about 0.20 pct.

A similar correlation was noted in the ductility properties of the pull bars. Table V compares physical property results of both grades of steel at the various residual silicon levels. When the residual silicon contents reached 0.20 pct a detrimental change took place. At this point the reduction of area of the grade B steel dropped from 51 to 46 pct while the reduction of area of the high tensile steel dropped from 50 to 34 pct. The examination of these bars with the 0.20 pct residual silicon showed that the inclusions were elongated or partly elongated instead of crystalline as was abserved in the heats with a 0.01 and 0.10 pct sicilon residual. In other words, with a 0.20 pct residual silicon the amount of aluminum and magnesium added was insufficient to either eliminate the pinhole porosity or to produce the correct type of inclusions.

When the silicon residuals were at a higher level insufficient aluminum was added to have any effect on the inclusions with the result that they were round as normally obtained when no special deoxidizers were added. Excellent ductility properties were obtained but the castings could not be classed as free of porosity.

This laboratory study indicated that the special deoxidizer investigated would be satisfactory

Fig. 1—(Left) Exograph of porosity test plate using aluminum treated steel.

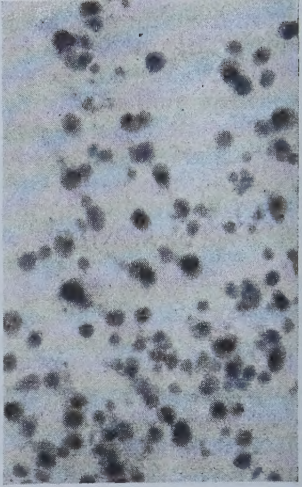

Fig. 2—(Right) Exograph of porosity test plate using steel with no special deoxidizer.

for use in basic practice where residual silicons are lower. It was found that the magnesium caused considerable pyrotechnics which would be objectionable. In order to remain on the safe side it was recommended that the aluminum content be increased and the magnesium content decreased. There is no doubt that this deoxidizer exhibits considerable promise and further work is contemplated.

Sodium

Sodium is one of the newer additions to steel which has aroused the curiosity of numerous investigators regarding its effect on sulphur reduction and deoxidization properties. A number of grade B and 0.45 pct carbon steel heats were produced in order to study its effect when added to liquid steel. Split heats were again used for comparison purposes. In some cases no special deoxidizers were added to the first half of the heat and sodium additions, as metallic sodium or as sodium emulsion in kerosene, were made to the second half of the heat. In all of the heats produced the sulphur, in the second half of the heats where the sodium addition was made, remained the same or was only reduced one point. Thus, it appears that under induction furnace melting the sodium addition made to the stream as it enters the ladle has no significant effect on sulphur reduction. There is a possibility that in large furnaces this condition might not be true. It should be added at this point that considerable sparking occurred when the sodium metal

Table V—Effect of Variations in Residual Silicon on the Physical Properties and Porosity Results of Steels Deoxidized with Si-Mg-Al Alloy

Steel	Residual Silicon	Porosity Results	Yield, Psi	Tensile, Psi	Elong., Pct	Red. Area, Pct
1	0.01	OK	48,400	75,600	30.3	51.2
1	0.10	OK	46,500	76,400	31.0	51.8
1	0.20	Some	49,000	79,000	29.3	46.8
1	0.30	Porosity	42,400	75,600	32.4	57.7
1	0.40	Porosity	45,100	78,300	33.5	57.7
2	0.01	OK	67,100	100,500	24.5	48.5
2	0.10	OK	67,600	99,100	26.2	51.3
2	0.20	Some	64,600	101,700	19.6	34.4
2	0.30	Porosity	65,400	104,700	20.8	40.2
2	0.40	Porosity	65,200	98,100	26.2	54.2

1—Grade B, 2—High Tensile

was added while very little sputtering occurred when the sodium emulsion was used. In the latter case a large amount of dense fumes were evolved due to the burning of the kerosene.

When the sodium was added in the emulsion form to grade B and 0.45 pct carbon steel it did not deoxidize the steel sufficiently to eliminate pinhole porosity as determined by our porosity test casting. The 1 lb of sodium added as sodium emulsion produced a test casting which was identical with respect to porosity as one poured in the first half of the heat where no sodium or special deoxidizer was added. This condition was found to be true in both grades of steel investigated. When 1 lb of metallic sodium per ton of charge was used pinhole porosity for all practical purposes was eliminated. This condition again was found to be true for both grades of steel under study. Thus it is our feeling that metallic sodium is a powerful deoxidizer.

Table VI—Comparison of Physical Properties of Steel Produced With and Without Sodium

Heat	Deoxidizer Per Ton, Lb	Yield, Psi	Tensile, Psi	Elong., Pct	Area, Pct	Charpy, Ft-Lb	
						70 F	—40 F
1	Al—2½ Graphidox-3	50,000	75,500	29.0	45.7	40.5	15.0
1'	Al—2½ Graphidox-3 Na Emulsion-1	49,800	77,600	30.5	51.6	38.0	17.5
2	None	51,000	94,600	24.7	45.0	20.0	3.3
2	Na Metal-1	51,000	90,400	19.2	25.5	14.8	6.3

1—Grade B Steel, 2—0.45 Pct Carbon Steel

In checking the physical properties of a few of the heats which were produced it was found that in the 0.45 pct carbon steel 1 lb of metallic sodium produced a metal with poor ductility properties. This was due to the fact that elongated inclusions were formed. When the sodium emulsion was used in conjunction with a regular aluminum addition on grade B steel an improvement in ductility properties was observed over the same steel without the sodium emulsion. Table VI compares the physical properties of the steels with and without the sodium additions.

In certain respects there appeared to be considerable promise for the use of this material but more investigations will have to be performed before consistent results can be expected on a production basis. Extreme care must be exercised in storing the metallic material, handling it and making the additions.

It is hoped that this paper has presented some information and ideas that may be of help in production problems and stimulate further research and investigations on this interesting and sometimes baffling subject of deoxidization. This opportunity is taken to thank the officials of the American Steel Foundries for permission to present this information and for the personal help and guidance of Mr. G. A. Lillieqvist, Research Director.

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[1] A. P. Gagnebine: Influence of Selenium on Sulfide Inclusions and Ductility of Cast Steel. *American Foundrymen's Society Transactions,* 1947.

British Report on Drop Forging

THE **"Productivity Team Report; Drop Forging,"** based on the findings of British forging experts after a tour of 130 American drop forge shops, 70 pct of which employ less than 200 men each, points up differences in practices and techniques in the two countries. The team deprecates the insistence in Britain of high quality regardless of forging use, pointing out that on some 20 forgings, American forge plant output will total as much as 400 pct more forgings per hr than British output.

In suggesting changes in British methods, the team recommended that the program be divided into two parts. Short-term and long-term policies were made, offering several recommendations. The short-term program should embrace maximum machine utilization; better cooperation on ideas and methods between forge plants; and better plant housekeeping to contribute to orderly production, raise efficiency and assist in recruiting suitable labor. Possibilities of shearing steel instead of the present practice of sawing or cutting should be studied; ventilation improved for worker comfort and efficiency; furnaces supplying hot stock should be improved and capacities increased; and descaling methods should be improved.

Larger hammers that will require fewer blows to produce a forging, result in less wear and tear on the plant and dies, and increase productivity were suggested, along with development of mechanical handling methods; a study of lubricants to eliminate their use where possible; an increase in the use of multi-impression dies; and recommended also were a systematic maintenance program to eliminate breakdowns; systematic tool and die and maintenance part storage systems; and the use of safety goggles, clothing and other gear.

On the long-range basis, the team recommended that new plants should be more spacious and well ventilated. Spaciousness allows the manipulation of work handling equipment, reduces handling costs, and allows grouping of items of plant equipment for better work flow. High speed, high capacity equipment must be installed where replacement is necessary. Full mechanization of working handling equipment is an ideal of the program.

Better planning of plant equipment was also emphasized, it being specifically pointed out that presses in the United States were often used to set and size forgings after clipping. This eliminates the necessity of passing the clipped forging back to the hammer for setting and enables the hammerman to maintain a continous rhythm of production. Improvement of product and development of new materials were emphasized, and the cooperation between maker and user of forgings was noted. Such cooperation often results in modifications in design that cuts costs. An educational and recruitment policy to develop skilled workers is also a vital long range policy recommended.

Stainless by Induction Melting

by R. J. Wilcox

WITH the expanding development of steels and alloys for special purposes, the use of the high frequency induction furnace for the melting of these materials has been increasing continually. While all grades of steel are melted in the induction furnace, including the plain carbon and the conventional low alloy steels, its greatest usefulness probably is found in the production of stainless steels, heat-resisting alloys, the newer cobalt and nickel base alloys for jet and aircraft applications, and some of the special tool steels. The induction furnace finds application also in connection with special casting processes, such as the centrifugal casting methods, where a selection of unit sizes lends flexibility to this process.

Induction furnaces vary in size from the small spark-gap laboratory unit up to approximately 4 ton motor-generator operated production units. The trend with this type of melting equipment has been toward small or intermediate size furnaces installed in batteries of two or more units, making available a frequent supply of metal in relatively short intervals of time.

Lining refractories may be either acid or basic, and the furnace may be designed for fixed position operation or portable operation where the entire furnace may be moved to the pouring location and used as a ladle. Most installations are of the fixed position type.

Operation at Michigan Steel Casting Co., Detroit, has been confined to basic lined, fixed position furnaces. Three furnaces are operated from a single motor-generator station having a capacity of 330 kw at a frequency of 960 cycles. Two of the furnaces are 1000 lb units and the third is a 100 lb unit.

The conventional basic linings consist of magnesia-alumina grain (Normagal) rammed in place dry, around an asbestos form to provide a crucible having a mean diam of 16 in. and a depth of 21 in. Sidewalls are 3 in. thick. Details of lining construction and burning-in practice were given in the 1946 Proceedings.

In melting nickel-chromium stainless and heat-resisting alloys, as much alloy scrap is used as is available. In practice this amounts to 80 pct of the total charge for 18-8 and related grades. This high percentage of scrap is made available at Michigan Steel Castings Co. by balancing scrap consumption between the arc furnace and induction units. Arc furnace heats have been standardized to use a total of 80 pct alloy scrap, 35 pct being returned shop scrap and the balance made up of remelt pig and other available scrap. The bulk of the shop scrap is therefore retained for induction melting. Identical grades of alloy are made in either arc or induction furnaces, depending upon the quantity, size of jobs, and molding areas.

Since induction furnace heats are substantially tailor-made heats consisting of a simple remelting operation, it is essential that all materials making up the charge are of known analysis. There is not sufficient available time in the melting of 1000 lb heats to make a chemical analysis of the melt before tapping.

Rigid precautions are observed to maintain the identity of all shop scrap by original heat analysis, if possible, and definitely by grade analysis. An off-analysis induction heat is the result usually of either an error in scrap or charging material identity or an error in arithmetic in charge calculation.

In the making of an 18-8 (type 304) heat, the nickel in the form of 9 in. square electrolytic cathodes usually is placed directly on the furnace bottom. This protects the bottom from dropping the balance of the charging materials into the furnace. The ferrochromium is added next, followed by the low carbon steel or Armco ingot iron component of the charge, and finally by sufficient alloy scrap to fill the furnace. The power is immediately turned on to maximum input. There usually is more scrap in the charge than can be placed in the furnace at a single

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charging and it is necessary, as melting progresses, to continue the addition of alloy scrap until the entire charge, with the exception of the ferrosilicon and ferromanganese, has been added. No ore or slag making materials are added.

After the nickel, Armco iron, ferrochrome, and alloy scrap are melted, the bath is heated to nearly tapping temperature. At this stage, usually there has accumulated a considerable slag covering. The power is turned off and the slag removed as cleanly as possible. The power is returned to the heat, the ferrosilicon and ferromanganese are added, and special degasification additions are made. Tapping temperatures of these alloys are usually from 3000° to 3200°F.

After the tapping temperature has been reached, a final degasifying addition of ferroselenium is made in the amount of ¼ lb of ferroselenium per ton. This addition is in the order of 0.0125 pct Se since ferroselenium contains an average of 50 pct Se. This practice has been found to be a definite insurance against gas porosity of the reducing gas type, frequently experienced from high hydrogen or nitrogen contents.

Selenium degasification has replaced former methods of combating hydrogen and nitrogen porosity, such as oxidation with ore during melting or the use of inert gas injections prior to tap. It is the result of considerable experimental effort in which it was found that minor quantities of selenium are extremely effective.

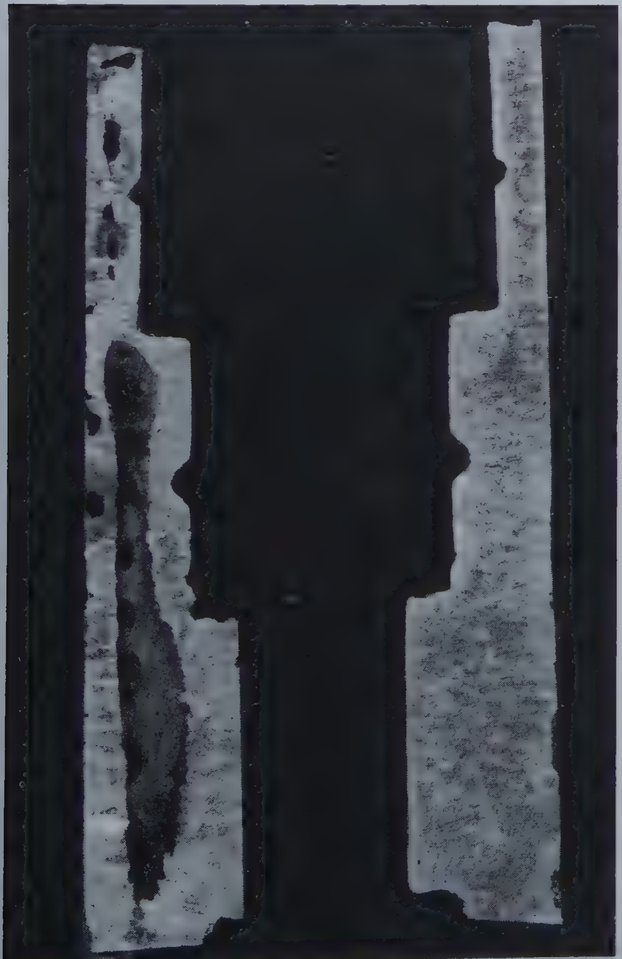

Fig. 1—Heat 336W: 18 pct Cr, 8 pct Ni alloy, Type CF-8. (Left) Casting poured with untreated metal. (Right) Casting poured from same metal treated with 0.01 pct Se. Specimens sectioned and microetched.

Extensive studies have been made to determine the effect of a minor selenium content on physical and mechanical properties, welding characteristics, and resistance to corrosion. No measurable effect exists on such properties with selenium up to approximately 0.10 pct Se.

Fig. 1 illustrates the striking effect of a small selenium addition in degasifying an 18-8 alloy, which was made with an intentionally high gas content. The heat was a 100 lb induction furnace melted alloy in which 100 pct scrap was dead-melted with small quantities of water added intermittently during melting. The tests were poured in green sand molds and the effectiveness of obtaining a high gas content is illustrated by the fact that the test casting poured from such metal was extremely porous.

After pouring the test casting with untreated metal, the balance of the heat was given an addition of 0.01 pct Se and an identical test casting poured. This casting was entirely free from gas porosity.

Operating data on the performance of the 1000 lb units in the production of 18-8 for castings are: Power consumption, 779 kwh per ton; melting time, 58 min per 1000 lb; average lining life, 110 heats per lining; and refractory cost, $4.41 per ton.

Experience with these units over several years operation indicates the following approximate recovery of the elements going into the make-up of the 18-8 type alloys: C, 100 pct; Cr, 99.0 pct; Ni, 100 pct; Mn, 90.0 pct; Si, 94.0 pct; Mo, 95.0 pct; Cb, 92.0 pct; and Se, 89.0 pct. (Due to slight losses in other elements, nickel final analysis frequently shows a higher quantity than original percentage composition calculated.)

The induction furnace is characterized by high alloy recovery. In certain heat-resisting type alloys, particularly the 35 pct Ni-15 pct Cr type, in which a carbon content of 0.40 to 0.50 pct is desired, a loss in carbon frequently is experienced on extended holding of the heat at high temperatures.

Induction furnaces find their greatest usefulness in the production of special steels produced to tailor-made requirements. Flexibility of operation is improved by being able to provide smaller quantities of metal at fairly rapid intervals of time, depending upon the number of units in a battery.

While high quantities of scrap can be utilized in induction melting equipment, it is important that it is all of known analysis. It should be noted that carbon reduction can not be obtained effectively in induction melting operations; and it is, therefore, essential that the carbon content of the charge does not exceed the maximum allowable range. This is in contrast to the arc furnace where higher carbon materials may be utilized by means of oxygen injection, and preliminary chemical analysis may be made on the melt to permit correction for any minor variables in scrap composition.

The development of selenium degasification has eliminated the past hazards of gas porosity and now renders these units capable of producing a dependable product with high scrap charges.

Slag Materials and Action

in Basic Arc Furnaces

by C. B. Post and
D. G. Schoffstall

THE standard basic electric arc furnace reducing slag generally is composed principally of lime, silica and fluorspar. Reducing agents can be added to the slag shortly after, or at time of fusion to speed up the removal of oxides, such as FeO, MnO, Cr_2O_3, etc.

There are several variations from this standard practice, such as the use of bauxite and other alumina-containing ganisters or clinkers which are designed to supplement all or part of the fluorspar content of the slags. In this paper only the standard lime, fluorspar, and silica slag are considered.

To serve as a basis of discussion, several requirements are noted for a reducing slag in the basic arc furnace. A slag must be able to be made reducing so that it can do its intended job of reducing the oxygen content of the bath; the slag must act as a dense enough blanket to protect the bath from atmospheric oxidation when solid deoxidizers are used; and it must protect the bath from oxidation when alloy additions are made so that accurate bath compositions can be obtained. A reducing slag also must be capable of reducing the sulphur content of the bath in addition to the oxygen content, since low sulphur contents are as much a characteristic of the basic electric arc furnace as low oxygen contents.

Burned lime is the basic raw material in these refining slags. The grade generally used is dead burned with a silica content of less than 3 pct, preferably magnesia less than 5 pct and alumina less than 1 pct. Such a dead burned lime will show a CO_2 content less than 3 pct, and a lime content of 90 pct. The moisture content of the dead burned lime is most important and care must be taken in packaging and transporting the burned lime from the kiln to the furnace floor, so that the lime is protected against atmospheric humidity up to the time of use. Hermetically sealed drums are used in addition to double-lined, waterproof bags with a cement seal in the inner bag and a woven wire seal on the outer bag. Also, hermetically sealed compartments are available, which seem to do their job in transporting larger quantities. It is desirable that the burned lime on the furnace floor be free of moisture. For 12 ft diam furnaces, the pebbled grade is desirable, and larger mesh will probably be used on the larger furnaces.

Fluorspar is unique in its fluxing action in lime-silica slags. To obtain the best action from fluorspar, it is advantageous to keep the silica content of the spar at about 6 pct. Silica less than 4 to 5 pct yields a fluorspar which is difficult to get into solution in the slag; by the time the spar gets fused into the slag, most of the CaF_2 will be lost. Silica contents greater than about 12 pct lead to significant pickup of silica in the slag, resulting in a glassy flat slag, difficult to handle in the furnace. As in the case of lime, it is necessary to guarantee the use of a spar with

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a low moisture content. Each individual plant has its own particular drying methods.

Most of the silica content of the slag will come from products of oxidation during the oxidizing period and from the spar, and depending on the age and temperature of the furnace, some amounts can be picked up from the furnace walls and roof by dripping. Some silica-sand additions are purposely made if the slag becomes too basic in character, especially near tap. Here, high grade silica sand, analyzing 99 pct SiO_2, can be used to cut the basicity and to make the slag more fluid and runny at the time of tap to promote runoff from the furnace hearth and to decrease ladle wall erosion. Crushed solid deoxidizers are generally thrown onto slag during or after fusion to facilitate removal of oxides, such as FeO, MnO, etc.

Crushed coke breeze is used in making up a white refining slag if the carbon content of the heat permits. Generally, there is a carbon pickup by the formation of calcium carbides in the slag. In the case of the smaller electric furnaces, the sulphur content of the crushed coke breeze does not present a problem because of the extremely high desulphurizing power of the white refining slags used, but the sulphur content might present a problem in large furnaces where high desulphurizing slags may be more difficult to obtain within a given time period.

Crushed ferrosilicon is commonly used either by itself or in conjunction with coke breeze to assist deoxidation of the slag. The ferrosilicon used is the same grade as that used in making alloy additions to the heats. Aluminum shot is also used to assist the deoxidation of refining slags on some grades of steel. Grade A aluminum is used in Carpenter Steel Co.'s shops and it is conceivable that if this grade were not used contamination of the bath could occur due to the alloy content of aluminum alloys used in recovering and making of off-grade aluminum.

Various proprietary compounds, such as calcium carbide, *Sil-X*, calcium silicon, etc., have been recently introduced for deoxidizing slags. In addition to their effect on deoxidation of the slag, attention must be given to the possible effect of the products of deoxidation of such compounds from the resulting fluidity and properties of a refining slag. This point will be further discussed.

A white refining slag must have the property of deoxidizing and desulphurizing the metal bath beneath it. This is accomplished by a migration of the oxygen from the bath into the slag where the carbon or graphite electrodes can reduce these oxides or where some of the deoxidizers can get to the oxygen in the slag. Desulphurizing is accomplished by a relatively large percentage of the lime being classified as free, in solution in the slag, but not tied up as a silicate, so that as the oxygen content of the bath is decreased, the sulphur can migrate from the bath to the slag and be tied up as calcium sulphide. It is to be noted that the migration of both oxygen and sulphur is dependent upon the interface between the bath and slag. If too much attention is paid to producing only a white reducing slag and no attention paid to its physical characteristics, such as fluidity, it is possible to obtain a good white slag that will absorb little, if any, oxygen from the bath. On the other hand, it is possible to get a slag that is not completely white, and containing about 2 to 3 pct iron oxide, which by the proper additions of either silica or spar can be made to have the proper fluidity and other physical properties required to wet the metal bath. In this case, absorption of oxygen is probably better than the highly viscous white limey slags which do little deoxidation on the metal. Carpenter's concern with refining slags has been more from the standpoint of their physical characteristics and effects on the metal bath than with chemical analysis.

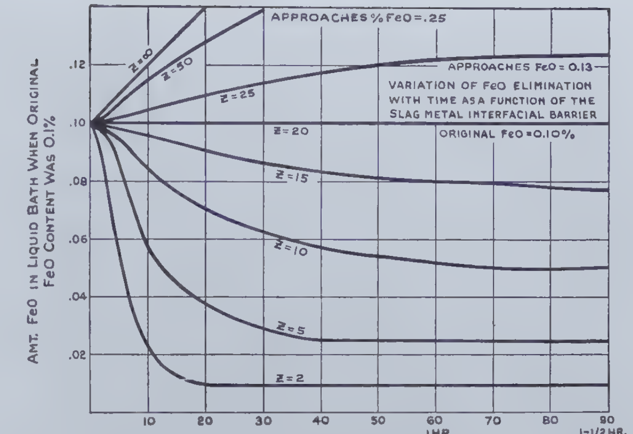

Fig. 1—Elimination of oxygen from basic electric furnace reducing slags.

The use of any material would be questioned, other than burned lime, spar and silica, in making up a slag as much from the standpoint of the effect of the compound on the physical properties of the resultant refining slag as on how much time the compound would save in turning the slag. To bring this point out further, the problem of slag action should be considered.

The problem of slag action is one of considering the pickup of oxygen from the hearth, the diffusion of oxygen into the slag, and the rate of reduction of iron oxide in the slag. The chemical equations are:

(1) $FeO\ (\text{in slag}) + 1/3\ \ CaC_2\ (\text{slag}) = 1/3\ CaO\ (\text{slag}) + 2/3\ CO + Fe\ (\text{liq})$

(2) $FeO(\text{metal}) \longrightarrow FeO(\text{slag})$

(3) $FeO(\text{hearth}) \longrightarrow FeO(\text{metal})$.

The solution to this problem in chemical kinetics, to be published at a later date, gives a quantitative picture of the elimination of FeO from the bath by slag action. In Fig. 1, the elimination of oxygen from the bath for an original FeO content of 0.100 pct at the time of making up the reducing slags and a pickup of FeO from the hearth of 0.0025 pct FeO per min is shown to be dependent upon the value of Ƶ.

$$\text{Ƶ} = \frac{\text{Absolute forward rate of FeO-CaC}_2\text{ reaction}}{\text{Specific diffusion rate of FeO from metal to slag.}}$$

The higher the value of Ƶ, the less the slag wets the metal and the slower oxygen is transferred from metal to slag. Low values of Ƶ mean a rapid rate of transfer of oxygen from bath to slag. Referring to Fig 1, if a bath starts off at 0.100 pct FeO at the beginning of the reducing period, a slag-metal interface characterized by

$Ƶ = 5$ will show a FeO content in the bath of 0.025 pct after about 40 min, while a slag-metal interface of $Ƶ = 10$ will show a FeO content of 0.05 pct after one hour. A slag-metal interface of $Ƶ = 20$ will just keep the bath at the same oxygen concentration even though the slag is completely reducing as far as cleanup of FeO in the slag is concerned. The sequence of operations upon which Fig. 1 is based will allow more definite statements to be made in the future on this question of wetting properties of slags, although it is too early to give definite values as yet. The problem is fundamental to basic electric arc furnace practice.

Up to the present time little or no information is available on satisfactory methods for measuring the viscosity of white reducing slags. This is difficult, since it requires a brief, articulate description of slags. Slag conditions can vary from a thick, viscous, limey slag which we believe serves little purpose to the bath because of a high resistance to transfer of oxygen from the bath; to a thin, watery slag composed of lime with high silica and spar contents where good wetting of the bath occurs, but where the slag is not able to support reducing conditions by the electrodes. There are also the carbide slags which can vary from a high carbide content down to a faint carbide odor when immersed in water. The heavy carbide slag can be extremely fluffy because of its high gas content, and also have an apparent low wetting property shown by the difficulty in slagging a spoon or in covering any surface with such a slag. The trend has been to get away from the high carbide slag types and to work to a faint carbide slag even on the higher carbon grades of steel. In Carpenter's shop, it is felt that the high carbide slags do not wet the metal sufficiently to affect good deoxidation of the bath. On analysis a good liquid faint carbide slag will contain 55 to 60 pct CaO, 15 to 25 pct SiO_2, 10 to 15 pct CaF_2, and about 10 pct MgO.

No worthwhile chemical figure can be given for the carbide content since this is a difficult sampling problem, but the carbide content is such that this slag will only show a faint carbide odor when immersed in water. In the case of low carbon, low alloy steels and stainless steels, it is preferable to work slags on the wet side for best reduction. Such slags will contain 50 to 60 pct CaO, 20 to 30 pct SiO_2, 10 to 20 pct CaF_2 and about 10 pct MgO.

The benefit from the two types of slag just described is derived from their physical property of wetting the bath at the slag-metal interface, perhaps more than from the individual components of the slag.

To summarize, it is felt that any discussion pertaining to slag-making materials in the basic electric arc furnace is chiefly a statement of elementary facts regarding the materials as follows:

1—The best grade of lime obtainable, used free of any moisture.

2—High-grade fluorspar, of about 60 pct SiO_2 content, free of contaminating elements such as Pb and Sn; or any feasible substitute which does not contaminate the metal bath and will still endow reducing characteristics to the slag.

3—Deoxidizing agents, proprietary or otherwise, which will not yield a product harmful either to the metal bath or to the physical condition of the slag.

4—The main problem is to choose the best materials available for the purpose, and decide what properties are necessary in the physical or chemical characteristics of the slag in the furnace to bring about the best refining action in the shortest time.

Russia Imports Strategic Materials

AMONG the strategic materials that Russia has been buying from the sterling area, according to *The London Economist,* machine tools have had the most attention. However, considerable quantities of tin, rubber, and wool likewise have been imported. While measuring Russian imports is guesswork, since U.S.S.R. publishes no statistics, *the Economist* estimated these imports on the basis of statistics from major exporting countries. The figures obviously are incomplete because shipments to any country of eastern Europe might eventually end in Russia.

Russia's imports of rubber have risen steadily since the war and reached a peak in 1949 of 105,000 tons, well over three times the prewar imports. During 1950 rubber imports may not exceed 85,000 tons. Until June, Russia seemed to be importing rubber at the rate of 50,000 tons per year, but since the Korean war buying seems to have been stepped up to about 100,000 tons a year.

Tin imports have been relatively high, the estimate being 600 tons in the first seven months in 1950 against 300 tons during the entire year of 1949. Russia is taking about four times as much wool as before the war.

The quantities of rubber involved do not seem alarmingly large to *The Economist* and do not suggest any serious attempt at stockpiling. Russia has an active synthetic rubber industry and can use the output from eastern Germany. As for tin, current imports are likely being consumed, although the sudden increase in the year's estimate suggests some accumulation taking place.

Chile Starts Operation of Integrated Steel Mill

The blast furnace has a capacity of 227,000 tons per year, and steel capacity is 260,000 tons per year.

CONSTRUCTION was started early in 1947 on the new steel works at Huachipato, Chile, under a team of engineers, Americans and Chileans with vast experience in construction of large industrial plants, and steel production was started in May, although the official opening will be in November.

The Huachipato plant was planned by the Steel Committee, appointed in Chile in 1942, and simultaneously by the Dept. for Steel of the New York Office of the Corporacion de Fomento. Actual design of the plant was entrusted to the H. A. Brassert Co. The Koppers Company was selected to participate in the administration of the Compania de Acero del Pacifico. A thorough check was made of the project, and the present plant is the result of collaboration of the best specialists of North America with Chilean engineers who have contributed with their knowledge and experience of local factors.

Chile possesses all of the necessary elements to create an iron and steel industry on a sound economic basis, such as a sufficient internal market, and an abundant supply of raw materials.

The blast furnace has an initial capacity of 227,360 tons yearly with a full capacity of 280,000 tons yearly. The yield of blast furnace gas will be used as fuel at the plant, and the slag will be used in the manufacture of cement. Steel will be produced in two Siemens-Martin refining furnaces, each with 84 tons capacity per loading, and one Bessemer converter with 17 tons capacity per loading. Initial consumption of iron ore will amount to 392,000 tons yearly, and will come from the Tofo mines near Coquimbo (Chile) by agreement with the Bethlehem (Chile) Iron Mines Co. Estimated steel ingot capacity is 260,000 tons annually.

Coal consumption for coke production will be 366,240 tons yearly, and about 10 to 20 pct of high quality American coal will be imported to assure production of high quality coke. 101,920 tons of limestone containing large amounts of practically pure calcium carbonate will be brought from deposits in the Madre de Dios Islands and used as the reduction flux. All other raw materials and supplies are assured, and most will be obtained within Chilean territory. The yards and docks will be provided with modern equipment for handling and warehousing of all raw materials.

A rolling and trimming billet mill will produce material for the bar and sheet rolling mill. Later a heavy structural shape and rail mill may be added. A bar and light section rolling mill, provided with a continuous heating furnace is designed to produce commercial bars, concrete reinforcing bars and light sections. The whole process is totally mechanized, and annexed to the mill will be a complete roll shop.

In the sheet steel plant, a discontinuously heated train will produce sheets up to 13 mm thick, 1.50 m wide and 5.50 m long. In addition to all kinds of laminated iron, pickled, galvanized, hot and cold rolled sheet, the plant will turn out welded steel pipe for water, gas and oil.

The plant in its initial stages is designed to produce round bars, for reinforced concrete; bars for extruding wire, forging, etc.; light structural forms (T, double T, angles, U, etc.); square bars, flat bars, platens, strip for welding pipe, hoops; bars for making bolts and nuts; light and heavy sheet steel, galvanized and pickled sheets and tinplate; pig iron and steel bars. At a later stage of development of the plant, rails and structural steel will be produced.

Byproducts will include coke gas for domestic and industrial fuel, benzol, light motor oils, creosote, ammonia water, foundry coke and coke for domestic use, and blast furnace slag for the manufacture of Portland cement.

Hydrogen Embrittlement of SAE 1020 Steel

by J. B. Seabrook, N. J. Grant, and Dennis Carney

Hot-rolled SAE 1020 steel, machined into tensile test bars was cathodically charged with hydrogen. Vacuum tin-fusion analysis provided accurate values of hydrogen at the desired moment. True stress-true strain tensile tests with and without aging of the test bars and at various strain rates indicate the role of hydrogen as an embrittling agent.

IT is unnecessary to review much of the literature on hydrogen embrittlement of steel since several excellent reviews and bibliographies exist.[1-3] Hot acid pickling and cathodic charging have been known to cause hydrogen embrittlement of steel and have been used as laboratory methods to charge steels with hydrogen.[4-8]

Experimental Procedure

The problem of prime concern in all instances, except in the work of Sims and coworkers,[10] is that at no time was there a definite known hydrogen value reported which could be related to a particular value of the degree of embrittlement. It was the purpose of this research to determine the relationship between hydrogen content and degree of embrittlement quantitatively.

The 1020 stock used for the specimens was hot-rolled 7/16 in. diam rod of the following analysis: 0.19 pct C, 0.40 pct Mn, 0.012 pct P, 0.036 pct S. Vacuum-fusion analyses for nitrogen and oxygen gave 0.014 pct O_2 and 0.0011 pct N_2.

Cathodic charging was used to cause embrittlement. The advantages of this method were that no quenching was necessary, the impregnation was reasonably controllable, and representative samples for analysis could be prepared simultaneously with the charging of the tensile bars.

Analyses for hydrogen were made in a vacuum-fusion type of apparatus which extracted gas from the samples by fusion in a molten tin-iron bath. This apparatus, which has recently been described in detail elsewhere, will not be discussed here.[11, 12] Consecutive samples can be analyzed every 15 min with an accuracy of 0.03 ppm. A sample from an electrolytic or pickling bath can be charged for analysis in about 3 min, and analysis completed in 15 min.

Samples of as-received 1020 stock were analyzed and found to contain a negligible amount of hydrogen (0.06 ppm).

Preliminary pickling and electrolytic charging gave highly variable results. Cold-worked samples showed higher values but ranged from 0.6 to 6.0 ppm of hydrogen. Charging at 90°C gave higher values of charged hydrogen, but troublesome films on many of the specimens resulted.

It was not until a few drops of a catalytic poison, prepared from 2 g of yellow phosphorus dissolved in 40 ml of carbon disulphide,[8] was added to the electrolytic cell that fairly consistent high values of hydrogen could be charged into the as-received 1020 steel at room temperature.

The cell used is sketched in fig. 1. The anode and fixture for the tensile specimens were fastened to the cell cover as shown, and the specimen was screwed in place, centrally located with respect to the anode. At first, anodes of lead and graphite were tried, but they contaminated the electrolyte and gave a slight deposit on the specimen. Later, a platinum wire was used in the form of a uniform helix. A current of 2 amp, corresponding to about 0.5 amp per sq in. of cathode, was used for most specimens. The electrolyte was 4 pct H_2SO_4 solution.

Fig. 1 shows the form of the special tensile bar, the main portion of which was an ordinary ¼ in. diam, 1 in. gauge length test bar, except that two to four small cylinders of stock were left attached by small links to the bottom end of the tensile bar for the purpose of providing samples for hydrogen analysis. Thus the bars and samples were charged with hydrogen simultaneously and an analysis could be made while the bar was being tested mechanically. Experiments were performed to determine how representative the test cylinders were of the middle of the test bar proper. While the bar center was being analyzed, the small cylinder was stored in dry ice, since it had been shown that such storage prevents loss of hydrogen for many hours.[12]

The results of these checks are shown in table I. The checks are very good (0.3 ppm) and indicate that it is permissible to use the small end cylinders to establish the hydrogen content of the tensile test bar proper.

Table I. Comparison of H_2 Content of Cylindrical End Samples and Centers of Tensile Bars, H_2 in ppm

Center of Bar	End Sample
1.3	1.5
1.5	1.8
3.2	3.1
4.6	4.3

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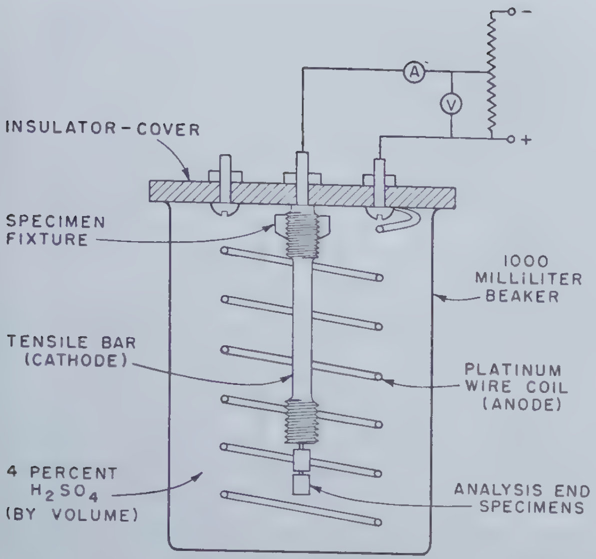

Fig. 1—Electrolytic cell arrangement for cathodic charging of hydrogen.

True stress-true strain tensile tests were made on the charged tensile bars. The true strain rate was kept as constant as feasible throughout the investigation (at 0.05 per min) except for the runs in which the effect of strain rate was examined. A rate of 0.05 per min gave a convenient length of test time in which to make strain measurements. By keeping the strain rate constant, the loss of hydrogen should have been more nearly the same in all the bars for the same amount of true strain.

A separate series of specimens with three cylindrical end samples attached were charged and held for various times after charging. Analysis of one end sample of each bar was made immediately after charging to establish the initial hydrogen content, and analysis of another sample from each bar was made at the time of the tensile test. Holding times of 6 min, 1 hr, 6 hr, and 24 hr were used before making some of the tensile tests; these tests are referred to as aged tests in this paper.

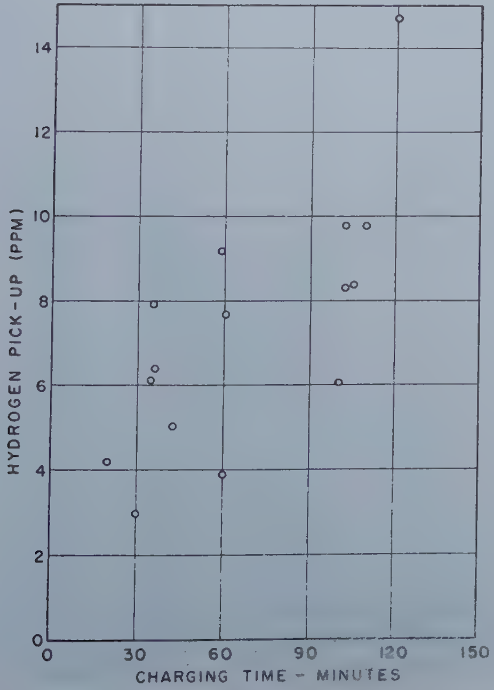

Fig. 2—Hydrogen pickup as a function of time of cathodic charging.

A series of bars with nearly the same high hydrogen content were pulled at different strain rates to check on the effect of strain rate. Rates of 0.01 to 6.0 per min were used.

Several specimens were cathodically charged for ½ hr, after which one portion was analyzed for hydrogen while another was placed under a mercury column to collect any evolved gas.

Finally, an attempt to detect an increase in hardness of fully charged specimens was made. A piece of the 1020 stock was charged to produce maximum embrittlement. Hardness readings were taken before and after charging along the same line of one flat side.

Experimental Results

Reproducibility of Cathodic Charging: Without the use of a catalytic poison, the maximum hydrogen charged in hot-rolled 1020 steel was about 3 ppm, but with a poison[8, 13] as much as 14 ppm entered the steel. Once it was apparent that a poison was necessary to achieve appreciable charging power in the cathode cell, tests were conducted to determine the reproducibility of the charging method. Fig. 2 shows the hydrogen values obtained for samples charged in a 4 pct H_2SO_4 solution, at room temperature, for various times. Analyses were performed in all instances within 3 min after cathodic charging.

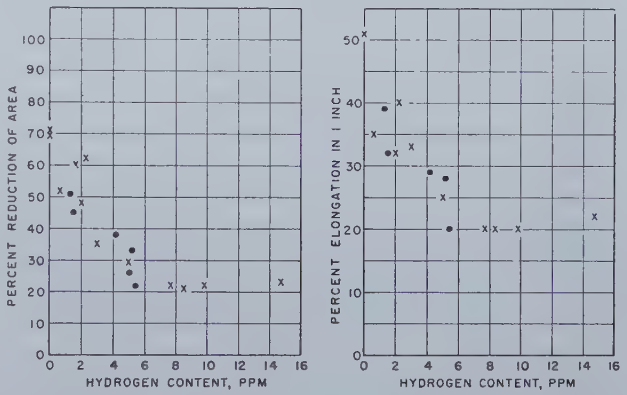

Fig. 3—Hydrogen content vs. elongation and reduction of area (from tensile tests).

x Tests pulled about 3 min after charging.
● Charged with >6 ppm of hydrogen, then aged up to 24 hr before testing.

Fig. 2 shows the rather poor reproducibility of charged hydrogen when time alone is used as a measure of the hydrogen content.

An attempt to check the usefulness of the technique of collecting hydrogen under a mercury column resulted in a value of 8 cc of gas per 100 g of metal which checked poorly against a value of 1 ppm (1.1 cc per 100 g) obtained in the analytical apparatus. Frequent large values of total gas led to the conclusion that the method of collecting gas under a mercury column is subject to frequent large errors and that the method is not always of analytical stature.

Effect of Hydrogen on Ductility in Tensile Tests: Fig. 3 shows the decrease in ductility (elongation and reduction of area) for charged tensile bars when such bars were tested about 3 min after charging (the *X* points). The ductility decreases sharply to a value of 20 pct elongation (and reduction of area) at about 5 to 6 ppm of hydrogen.

For hydrogen contents greater than about 6 ppm, no further decrease in ductility occurs. These data are in good agreement with the results of Sims et al.[12] A second set of test bars was charged to contain greater than 6 ppm of hydrogen (maximum embrittlement) but were permitted to age at room temperature in air for up to 24 hr before testing. The ductility values from these tests (plotted as ● points) fit essentially the same curve that satisfies the unaged tests.

In none of the tests shown in fig. 3 was there evidence of an embrittled outer zone. The fractures were uniform across the cross-section but differed from each other as the degree of embrittlement increased.

Rate of Hydrogen Evolution: Fig. 4 shows the values of retained hydrogen as a function of the original charged hydrogen content and the holding time at room temperature. Since four analytical end specimens at the most were available, the number of analyses which could be run was limited. The drop-off is very rapid during the first 3 or 4 hr, after which the remaining hydrogen diffuses out very slowly and is not all out after 72 hr. Apparently the rate of loss of hydrogen is not entirely dependent on the original or charged hydrogen. In two instances there appeared to be a holding period. A sample with 9.2 ppm initially was losing hydrogen more slowly after 4 hr than a sample originally containing 4 ppm.

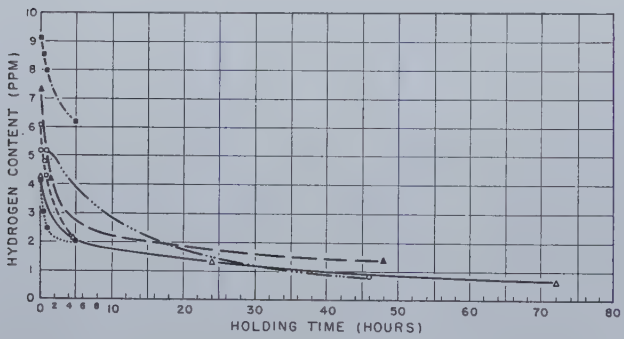

Fig. 4—Hydrogen evolution at room temperature as a function of holding time. Linear coordinates.

In view of the very high rate of hydrogen loss usually observed during the first half hour after charging, it is obvious that analysis must be performed in the shortest possible time after charging. Even a 5-min hold after charging may result in an appreciable loss of hydrogen.

True Stress-True Strain Relationships and Hardness: True stress-true strain plots are shown in fig. 5. Data for all the specimens are not plotted, but typical results are shown. Points for untreated and low hydrogen specimens fit one curve, while high hydrogen specimens gave a curve somewhat above this, as shown.

It is observed that higher true stress-true strain curves are found for the high hydrogen specimens. Hardness tests which were made less than 1 min after charging failed to show any hardness increase in the most embrittled test pieces, even including those showing surface bursts. Since the higher hydrogen test bars were as much as 6000 psi (in engineering tensile strength) above the untreated and low hydrogen curves, this difference in tensile strength indicates there ought to be a hardness difference of about seven Rockwell B points, using the usual relation between tensile strength and hardness.

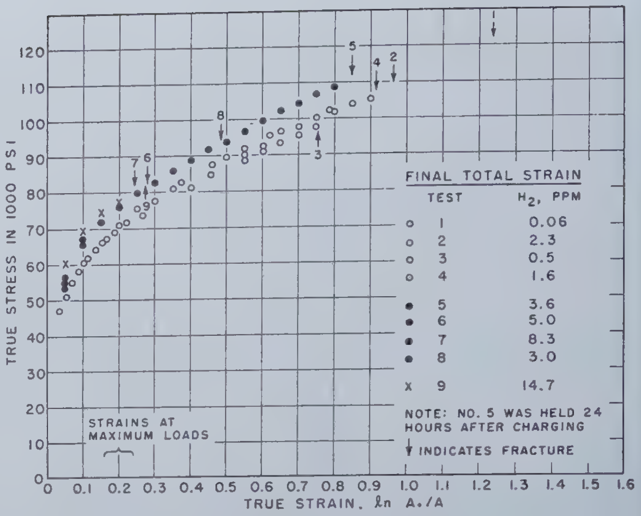

Fig. 5—True stress-true strain tensile curves for various hydrogen contents.

Halves of two tensile bars, one untreated and one embrittled the maximum amount, are shown in fig. 6. It may be seen that the embrittled bar surface is covered with small bursts and pimples. Not all of the embrittled and not all of the high hydrogen specimens had such surfaces, but all of those that did contained more than 4 ppm of hydrogen. Several specimens had tiny pimples on the surface as soon as a few seconds after removal from the cell.

Micrographs of bursts from embrittled specimen are shown in fig. 7 where it may be seen that surface metal was literally exploded outward. Such ruptures were found at the surface all along the specimen. In fig. 7*a* a rupture may be seen which apparently occurred within a ferrite grain. This location of ruptures well within ferrite grains was observed in many instances. Otherwise, the ruptures and fractures could not be classed as intercrystalline or transcrystalline.

Effect of Strain Rate on Ductility: Results of the variable strain rate tests on the reduction of area values are plotted in fig. 8. All test bars were initially

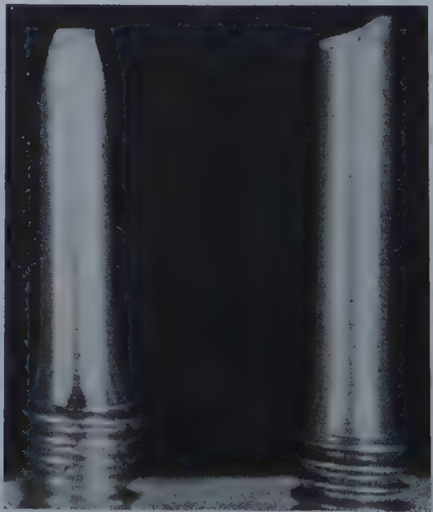

Fig. 6—Halves of untreated and hydrogen impregnated specimens. X2.

charged with greater than 6 ppm of hydrogen (maximum embrittlement). For these high hydrogen specimens, the ductility was not a function of the true strain rate at low rates, but an appreciable effect was indicated for the fastest rates obtainable on the tensile machine. This is contrary to previously reported work.[9]

The strain rate data show that over the usual range of testing speeds there is no large effect of strain rate for this steel. At very high strain rates (in the neighborhood of 5 to 10 per min), the embrittling effects of hydrogen are minimized. This strain rate effect suggests why hydrogen embrittlement has not been detected in impact tests.

Discussion of Results

The presence of hydrogen, probably as monatomic hydrogen, does not of itself guarantee embrittlement as evidenced by the following:

1. There is no increase in hardness as the hydrogen in the hot-rolled steel increases.
2. There is no permanent damage to the hot-rolled steel due to an initial high hydrogen content. Fig. 3 shows that the ductility can be recovered, if the hydrogen diffuses out.

Under conditions of strain, however, the hydrogen can cause embrittlement. The initial absence of a hardness increase but the evidence of a maximum stress increase supports this idea (fig. 5). Possibly the hydrogen may do this by forming molecular hydrogen under conditions of strain, and by segregating at or in defects causing large pressures to be exerted.

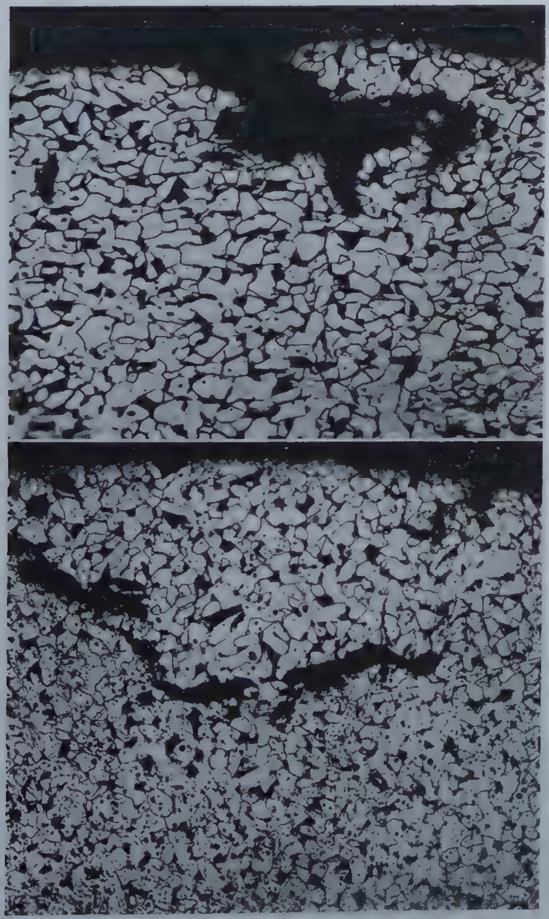

Fig. 7—Micrographs of embrittled specimen. X100. *a*, **upper;** *b*, **lower.**

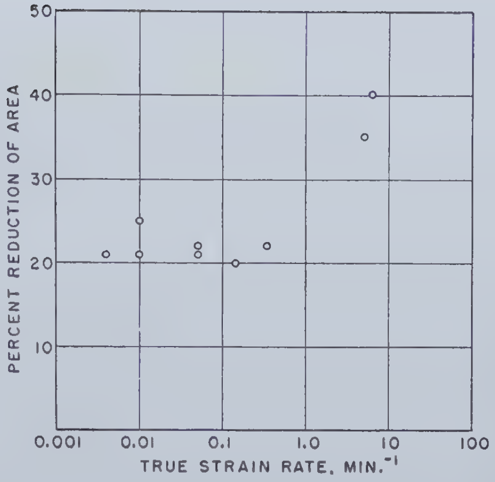

Fig. 8—Reduction of area vs. true strain rate for test bars having greater than 6 ppm of hydrogen.

The strain rate tests further indicate that at very high strain rates, the hydrogen does not have time to diffuse and combine into molecular hydrogen. As a result, the higher strain rate tests show very little embrittlement. Strain rates approaching the impact rates would show no embrittlement, whereas the slower tensile test strain rates show maximum embrittlement.

Conclusions

For this hot rolled 1020 steel:

1. Cathodic charging of hydrogen aided by an electrolyte poison, is rapid but is not readily reproducible, based on time of charging alone.
2. There appears to be no permanent damage to the metal lattice of an annealed steel by high values of charged hydrogen, and the mechanical properties are dependent on the actual hydrogen content at the time of the test.
3. At about 5 ppm of hydrogen, a minimum is reached in the elongation and reduction of area.
4. Hydrogen diffuses from the charged samples rapidly during the first 3 or 4 hr but is not all out after 72 hr. The initial hydrogen content does not appear to control the rate of hydrogen loss.
5. True stress-true strain curves show small changes with increasing hydrogen. There is a gain of about 6000 psi in engineering tensile strength, but this is not indicated by prior hardness measurements.
6. As the strain rate increases less embrittlement is noted. At rates of less than about 0.5 per min, maximum embrittlement results; whereas at rates greater than about 5 per min, it appears that progressively less embrittlement will be noted.
7. It is indicated that a certain minimum strain is necessary to cause embrittlement in hydrogen containing steels. This strain is greater than the elastic or yield strain for 1020 steel.

Acknowledgment

The authors wish to express their thanks to the Office of Naval Research for support under contract N5ori-78 Task XVI, NR-031-186, which made this research possible.

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Technical Notes

Hydrogen Elimination by Aging

by C. E. Sims

IN an earlier paper by Sims, Moore, and Williams,[1] data were given to show that hydrogen contents of 0.3 relative volume (0.00033 wt pct), existing at the center of 4-in.-square cast-steel coupons, could be removed by aging at 400°F for 125 hr. At the end of that time, complete restoration of normal ductility for the steel was obtained. Replicate specimens of the same steel were aged at room temperature up to 555 days or 18½ months. At the end of that time, the hydrogen content at the center had fallen to 0.13 relative volume or 0.00015 wt pct, but there was no perceptible change in the ductility.

On the basis of experience with accelerated aging of 1-in. and 4-in. coupons and room temperature aging of 1-in. coupons, it was predicted that, some time after two years and when the hydrogen content has been reduced to about 0.10 relative volume, there would be some recovery of ductility. One set of three bars remained, and these were held for 1310 days, or more than three years. Then tensile test bars were cut from the center, and these bars were sampled for hydrogen analysis at the time they were broken. The sample specimens were cylinders ⅝ in. in diam x 1¼ in. in length. The data showed that in this time the average hydrogen content had fallen to 0.096 relative volume or 0.00011 wt pct, and the ductility had increased sharply. Elongation had risen from 10 to 17.3 pct, while reduction of area increased from about 16 to 27.5 pct. On the basis of these data, fig. 1 was drawn to replace fig. 15 of the earlier paper. Extrapolation of the curves of fig. 1 indicates that it would require a period of about 2200 days or approximately six years at room temperature to reduce the hydrogen to the minimum value and to recover full ductility in the center of the coupons.

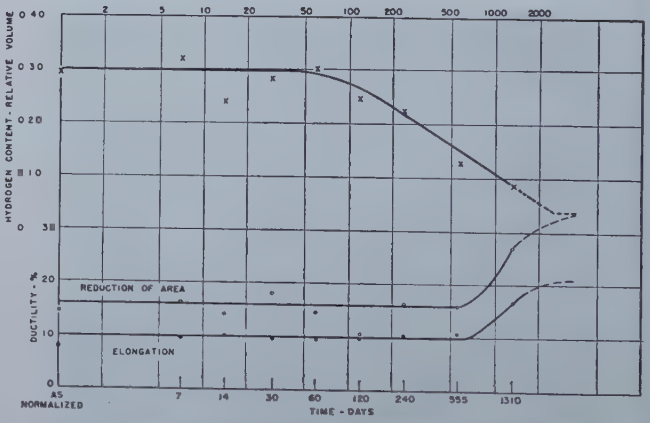

Fig. 1—Change in hydrogen content and ductility with time for center of 4-in. coupons aged at room temperature. Data plotted are averages of three tests.

The aging process apparently involves the movement of hydrogen from the interior to the surface of the bar and evaporation at the surface. This flux of gas presumably follows some diffusion mechanism, and an effort was made to use the aging data, obtained at room temperature and at 400°F, to calculate coefficients of diffusion, in the hope that they might indicate the nature of the diffusion. The conclusion was reached, however, that the data were inadequate for such a purpose.

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TN 46 E. Manuscript received Sept. 5, 1950.

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A Simple Torsion Pendulum for Measuring Internal Friction

by M. E. Fine

IN the apparatus for measuring internal friction shown in fig. 1, a modification of that described by Kê,[1, 2] the parasitic energy loss or background is equivalent to a Q^{-1} of approximately $4x10^{-5}$. This low value of background was obtained by using a jeweler's collet of appropriate size for the upper support, eliminating lateral motion without immersing the bob in oil, and designing the bob to reduce air resistance. The pendulum is supported on the frame through a snug fitting, sliding rotary joint (fig. 1-B). A slight twist of the top imparts essentially pure torsional motion to the pendulum. No evidence of energy loss in the sliding joint has been observed. In the bob (*E*) steel balls are used in the torsion arm, and the bottom is filled with lead giving a total weight of 94 g. A lighter bob may be used for small diameter specimens. Another bob was a solid disc with provision for adding discs to change the frequency. The oscillating image of the filament is recorded on a revolving drum camera (fig. 1-*J*) driven by a synchronous motor. This allows use of frequencies higher than can be measured visually on a glass scale.

Samples varying in diameter from 0.020 to 0.075 in. have been measured, the frequencies have ranged from 1 to 12 cps, and the maximum strain varied from 0.5 to $10x10^{-5}$. With appropriate modification the sample may be placed in a thermostat.

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Table I. Internal Friction of Metal Wires

Material	Diam In.	Freq. cps.	Max. Strain	Internal Friction Q^{-1}
Beryllium-copper solution treated	0.058	6.4	1.2x10-5	$6x10^{-5}$
Same, age hardened	0.058	6.6	1.2	5
Nickel brass, hard drawn	0.065	7.9	1.7	10
Same, 1.5 mil, lead coating	0.068	8.1	1.2	49
Permendur (50Fe,50Co,0.5Mn) slowly cooled from 1000°C	0.063	10.9	3.5	350
Same	0.063	10.9	1.3	99
Same	0.063	1.1	3.5	290
Permendur quenched from 1000°C	0.063	12.4	2.1	17
82Mn, 18Cu, quenched from 925°C, aged 1 hr at 400°C	0.061	5.1	1.0	1,750
46.8Ni, 0.5Mn,Bal.Fe, cold worked	0.074	11.4	1.7	20
Same, annealed at 900°C	0.074	11.9	1.3	59

The apparatus may also be used to measure the shear modulus.

In the examples of measurement given in table I the internal friction of Permendur and the 46.8 Ni-Fe alloy are due, for the most part, to magnetomechanical hysteresis[3] (elastic hysteresis accompanying stress-induced magnetostriction) which depends on strain amplitude and increases with annealing. The internal friction of most materials decreases with annealing.

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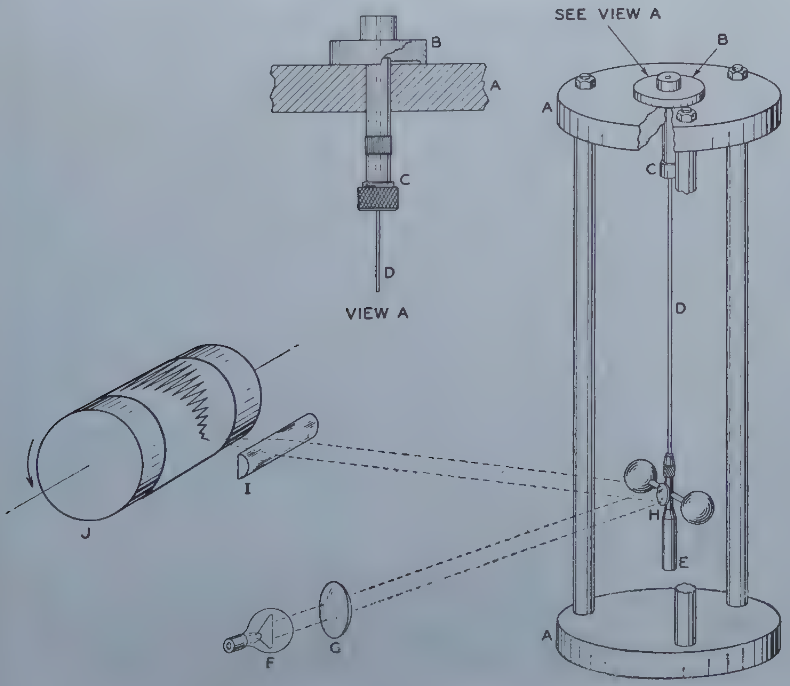

Fig. 1—Torsional pendulum for measuring internal friction.

A	**Frame**
B	**Slip joint**
C	**Jeweler's collet holder with replaceable collet**
D	**Specimen**
E	**Bob with torsion arm**
F	**Light source**
G	**Lens**
H	**Mirror**
I	**Cylindrical lens**
J	**Rotating drum camera**

Effect of Rate of Freezing on Degree of Segregation in Alloys

by William T. Olsen, Jr. and Ralph Hultgren

WHEN a liquid alloy freezes, the solid first formed usually differs widely in chemical composition from that last formed, so that there is segregation in the alloy as cast. For example in the copper-nickel system (fig. 1) the first solid formed from a liquid containing 55 atomic pct Cu may contain as little as 38 pct Cu, while the last must contain well over 55 pct.

Three factors may act to decrease segregation from the maximum possible.

1. Diffusion in the cooling solid tends to make the phase homogeneous, decreasing segregation. This may be important at slow rates of cooling.
2. Segregation is impossible without diffusion in the liquid. At extremely rapid rates of cooling there may not be enough time to allow maximum segregation.
3. Supercooling delays nucleation to temperatures well below the liquidus thereby decreasing segregation. Hence the first nucleus in the copper-nickel system may contain well over 38 pct Cu. At sufficient supercooling the first nucleus may form below the solidus, in which case there is no reason to expect any segregation whatever.

From these considerations, we could predict that at sufficiently low rates of cooling the alloy would be unsegregated because of factor 1 and at sufficiently high rates of cooling there should also be no segregation because of factors 2 and 3. Considerable segregation should occur only at intermediate rates of cooling.

We have demonstrated experimentally that segregation can be completely suppressed by rapid rates of cooling. For the alloys studied, however, these rates are too great to be attained in any commercial practice.

An alloy of 55 atomic pct Cu, 45 atomic pct Ni was frozen by cooling at varying rates. The degree of segregation in the solid was determined by X-ray diffraction photographs. Slow rates were obtained by slowly cooling the furnace containing the liquid alloy; fast rates by pouring or ejecting droplets of the alloy into water or iced sodium hydroxide solutions. The cooling rate of the droplets can be calculated from their dimensions by assuming reasonable values of thermal conductivity.[1] The experiments were repeated with an alloy of 16.5 pct Cu and 83.5 pct Au. A single experiment also showed a 50 atomic pct Bi-Sb alloy had no segregation at the most rapid quench.

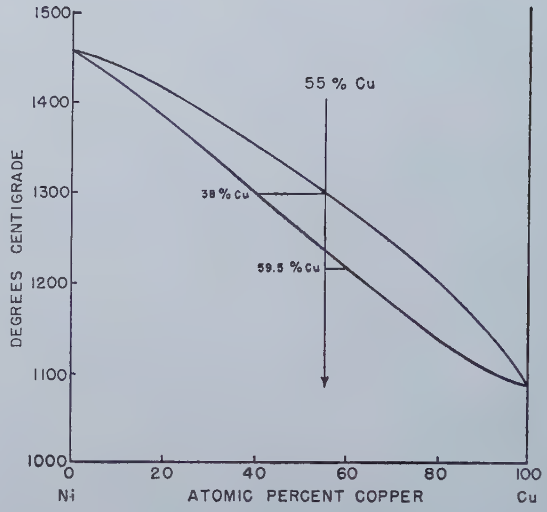

Fig. 1—Cu-Ni system.
Metals Handbook, 1948.

Table I. Effect of Rate of Cooling on Segregation

Composition of Alloy, Atomic Pct			Rate of Cooling, Deg C per sec	Composition Range, Atomic Pct Cu	
Cu	Ni	Au		First to Freeze	Last to Freeze
55	45		0.0055	38	59.5
			5,700	44	59.5
			13,300	46.5	59.5
			97,000	55	55
16.5		83.5	0.0055	16	18.5
			4,325	15	18.5
			11,100	13	18.5
			61,600	16.5	16.5

The position of back-reflection X-ray diffraction lines is a highly sensitive function of the lattice constant, which in turn depends on the chemical composition of the phase. A phase of varying composition will give broad diffraction lines. By measuring the edges of these lines and making suitable corrections for intrinsic line width, it is possible to determine the range of lattice constants represented. These can be converted to chemical compositions from a lattice constant vs. composition curve. Results are shown in table I.

In the copper-nickel system the greatest segregation is found at the slowest cooling rates, where the lowest percentage of copper theoretically possible is found. In the copper-gold system, on the other hand, the degree of segregation is decidedly less at the slowest rates of cooling, being greatest at 11,100°C per sec. At no rate is the theoretically lowest percentage of copper (12 pct) found.

At the rates of cooling found in sand and die castings the degree of segregation is large and depends little on the rate of cooling.

Acknowledgment

Most of the material in this paper is abstracted from a thesis presented by William T. Olsen, Jr. in 1948 in partial fulfillment of the requirements for the degree of Master of Science at the University of California.

W. T. OLSEN, JR., University of California, Berkeley, Calif., and R. HULTGREN, Member AIME, is Professor of Metallurgy, University of California.

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The Formation of Annealing Twins

by J. E. Burke

Although annealing twins are prominent only in recrystallized metals, deformation is not necessary to produce them. Rather, annealing twins may form whenever a grain boundary migrates. The broad annealing twins found in coarse-grained metals are all formed after recrystallization is complete.

THE origin of so-called annealing or recrystallization twins in face-centered-cubic metals continues to be a matter for speculation, and in the present report an attempt is made to explain their origin and to account for at least a majority of the observations concerning their behavior.

The fact that annealing twins are prominent only after recrystallization suggests that deformation may be necessary for their formation. In 1926, Mathewson[1] reported the observation by Phillips that annealing twins are frequently parallel to strain markings which delineate octahedral planes in the deformed (and partially recrystallized) matrix, and suggested that strain markings are mechanical twins which grow into annealing twins during recrystallization. Later work by Burke and Barrett[2] has shown that strain markings are traces of planes upon which slip has occurred, and that there is no evidence for the formation of mechanical twins of microscopically resolvable width in face-centered-cubic metals. Mathewson[3] has pointed out, however, that slip may produce twin faults, and later modifications of this hypothesis have assumed that twin faults rather than true mechanical twins serve as the nuclei for annealing twins.

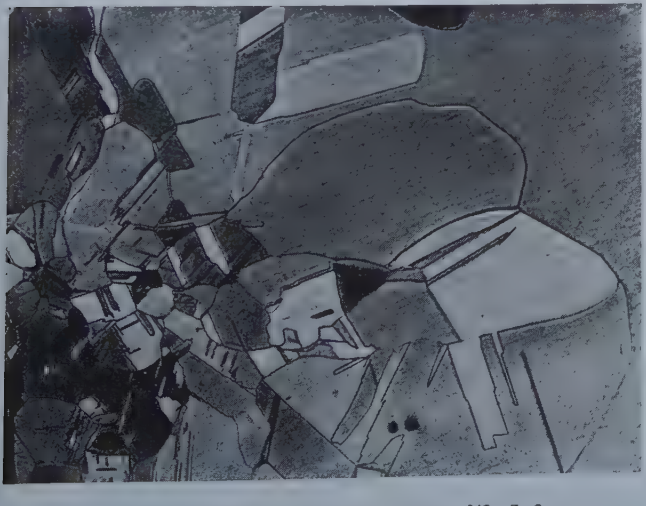

Fig. 1—Single crystal of alpha brass with deformation gradient. X100.

The specimen was deformed 8 pct in compression and then indented over the lower left-hand corner in a Rockwell indenter, and then annealed to cause partial recrystallization. Note intense twinning in heavily deformed part and slight twinning in less deformed part. The upper right-hand corner is unrecrystallized. Area reduced approximately 25 pct for reproduction.

Carpenter and Tamura[5] suggested, also in 1926, that annealing twins might form by accidents of growth. A close-packed layer of atoms can be added to the octahedral plane of a face-centered-cubic metal in two possible positions, the right position

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continues the original orientation, the wrong one forms the first layer of a twin. The wrong positions are identical as far as the distance to nearest neighbors is concerned, although the distance to second nearest neighbors is slightly changed. One concludes from this as well as from numerous other observations that the energy associated with such a twin interface is small, and thus that it would not be difficult to form. If during the migration of a grain boundary a few atoms were to fall into the wrong set of positions, the first layer of a twin would be formed, and if conditions were favorable to its growth the twinned orientation would propagate itself to give a twin of detectable width. A second error in positioning on an octahedral plane parallel to the first would restore the original orientation and produce a parallel-sided twin band. This mechanism indicates that twins can form whenever a grain boundary migrates, and that the number and width of twins formed would be controlled solely by the frequency of accidents.

Evidence Supporting the Mechanical Nucleation Hypothesis

Recently, Maddin, Mathewson, and Hibbard[6] have obtained evidence which supports the mechanical nucleation hypothesis and which is more specific than the observations that annealing twins form in recrystallized metals and that they are frequently parallel to strain markings in the matrix. They carefully deformed a single crystal in tension and found that all the recrystallized grains produced by annealing had an octahedral plane in common with the parent grain, although otherwise their orientations were different. The octahedral plane was always a plane upon which slip had occurred, and it served as the composition and twinning plane for annealing twins in the new grains. Only annealing twins which fulfilled this condition were found.

Kronberg and Wilson[7] found that the intensity of twinning in deformed and recrystallized cube-texture copper is greater than that in cube-texture copper which has undergone spontaneous secondary recrystallization without deformation.

The number of twins per unit volume (although not necessarily the number per grain) is greater in material which has been recrystallized following a heavy deformation than that in metal which has been recrystallized following a light deformation. An example of this is shown in fig. 1, which is a single crystal of brass reduced 8 pct in thickness by compression and then indented in the lower left-hand corner of the field shown. After partial recrystallization, small profusely twinned grains appear in the region which was heavily worked by the Rockwell impression, while in the less deformed periphery, the twins are larger and less frequent.

These observations all support the hypothesis that twin faults produced by deformation may play a role in the formation of annealing twins, although they do not indicate by what mechanism the twins grow from the twin faults.

Evidence for the Growth Fault Hypothesis

There are other observations of the properties or behavior of annealing twins which are difficult or impossible to explain by the mechanical nucleation hypothesis, but which are readily explained by the accident of growth proposal. Some of these ar discussed in the following sections.

Existence of Several Twin Families in a Single Grain

Recrystallized grains almost invariably have a different orientation from the parent grain, although frequently the parent and daughter grain have an octahedral plane in common. The evidence presented above indicates that a twin fault in the matrix on this common plane can nucleate twins in the daughter grain with the common octahedral plane as the twinning plane. Although twin faults may have been produced on several of the octahedral grains in the matrix, only those on the common octahedral plane can operate to nucleate annealing twins in the daughter grain, thus one can explain the appearance of only one family* of annealing twins in the daughter grain by the mechanical nucleation hypothesis.

One finds frequent examples, however, of a single grain which shows several families of twins, and Hibbard, Liu, and Reiter[8] report that the average grain in alpha brass has almost two twin families. One could possibly explain this by assuming that during recrystallization the growing grains feed on several deformed grains of different orientation, which happen to have faulted octahedral planes parallel to different octahedral planes in the growing grains, but many cases exist where this explanation cannot apply. The grains growing in the single crystal in fig. 1 frequently show several twin families. Fig. 2 illustrates the fact that several twin families may be formed very early in recrystallization. The tiny recrystallized grain growing in alpha brass has at least three twin families, and none of these are parallel to, and thus could not have been nucleated by, twin faults on the slip planes which can be seen in the matrix.

Annealing twins thus appear with such orientations that they could not have been nucleated by mechanically induced twin faults. They could have been produced by accidents of growth, however, and

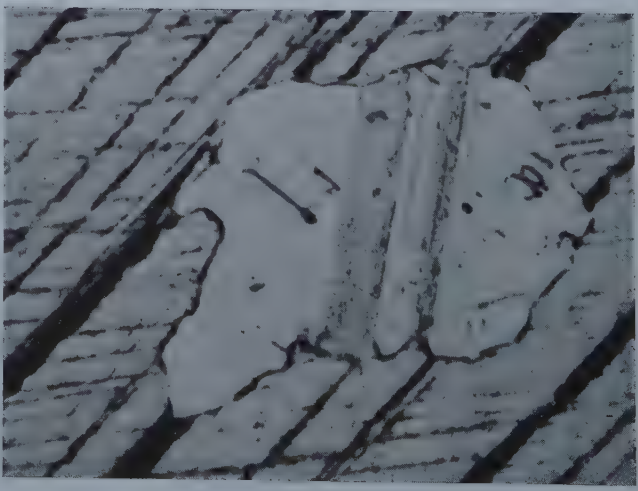

Fig. 2—Tiny crystal growing in deformed matrix. X2000.

Three twin families are displayed in the new grain and none of them are parallel to the two families of octahedral strain markings in the unrecrystallized matrix. Area reduced approximately 25 pct for reproduction.

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* Any one of the four sets of parallel octahedral planes can serve as twinning planes. All of the twins which use one set of octahedral planes as a twinning plane belong to one family.

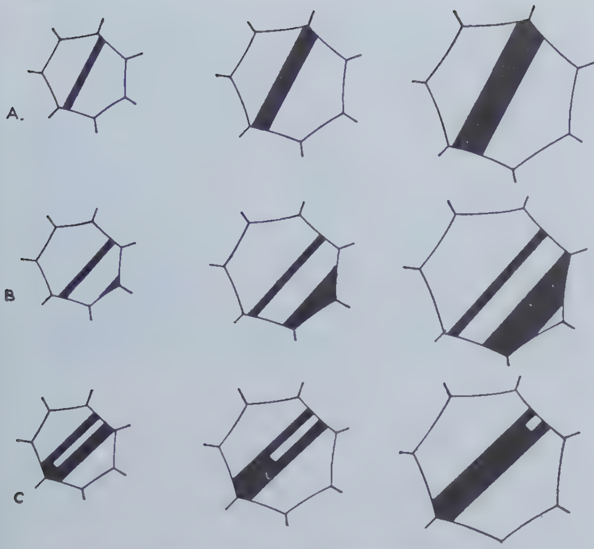

Fig. 3—Three possible mechanisms for twin broadening.

A—Lateral twin boundary migration.
B—Formation of new twins.
C—Coalescence. See text for detailed discussion.

the existence of several twin families in a grain supports this hypothesis.

Apparent Broadening of Twins During Grain Growth

The average width of parallel-sided twin bands in a coarse-grained metal is much greater than in a fine-grained specimen; indeed, in the coarse-grained case the twin bands may be many times wider than the diameter of the largest grain in a fine-grained specimen of the same material. One explanation of this fact might be that twin boundaries migrate in a direction perpendicular to the twinning plane during grain growth, as illustrated in fig. 3*a*. This broadening mechanism must operate if all annealing twins are nucleated by deformation and formed at the time of recrystallization, as postulated by the mechanical nucleation hypothesis.

The growth-accident hypothesis suggests that broad twins may be formed in the manner illustrated in fig. 3*b*. A twin can grow broader by simple grain boundary migration if one side of the twin forms the boundary of the grain. It can be terminated by a second twinning act on a plane parallel to the original twinning plane, and with further grain growth it will develop into a parallel-sided twin of typical appearance. The width of twins formed in this way will be inversely proportional to the frequency of twinning on that twinning plane, and the wider bands in a coarse-grained specimen would be the result of a decrease in twinning frequency with increase in grain size.

The second mechanism is more appealing because it seems unlikely that twin boundaries can migrate perpendicular to the twinning plane. It is true that there are possible driving forces for perpendicular migration, such as the reduction of the total length of the coherent twin boundary and the presentation of a more favorable orientation to adjacent grains as suggested by Smith.[11] Nevertheless, it is difficult to understand how a twin interface could migrate past an inclusion. An ordinary grain boundary is retarded in its migration by an inclusion, but it can usually get past it by bending and reforming on the opposite side while continuously decreasing its area. The low energy of a twin boundary is associated with the identity of the composition and twinning planes, however, and it cannot bend without increasing its energy to an amount comparable with an ordinary grain boundary.

To determine whether or not migration of twin boundaries perpendicular to the twinning plane can occur, a number of fields were photographed on a polished surface of a high-purity brass, and the same fields were photographed again at stages during annealing to cause grain growth. A typical field is shown in fig. 4. Examination of the series shows that the width of twin bands bounded by parallel sides remains unchanged, thus confirming the prediction that straight twin boundaries would not migrate perpendicular to their surface. Twins having a grain boundary as one side do grow wider, however, and several examples may be seen of the formation of broader twins with parallel sides by the mechanism illustrated in fig. 3*b*.

It is interesting to notice that annealing twins usually form at or near the corners of grains, although there is no obvious reason for this. An excellent example, where three families of twins have recently appeared at three different corners of the grain, is presented in fig. 5.

It has already been mentioned that the thickness of annealing twins is controlled by the number of times the twinning act occurs for a given distance of grain boundary migration. In heavily cold-worked metal which has been recrystallized, the

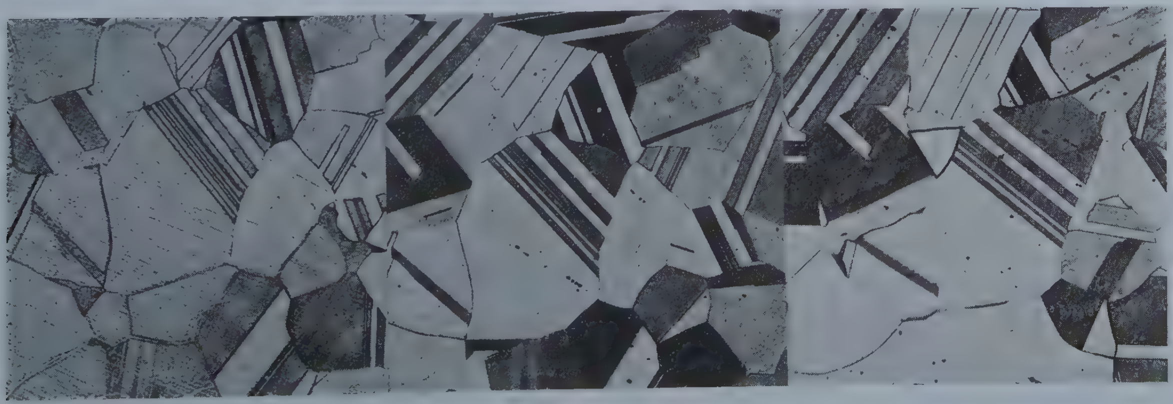

Fig. 4—Alpha brass. X75.

Same field at three stages of annealing. Twin boundaries do not migrate laterally unless they coincide with grain boundary. Third twin from the left in large central grain shows coalescence.

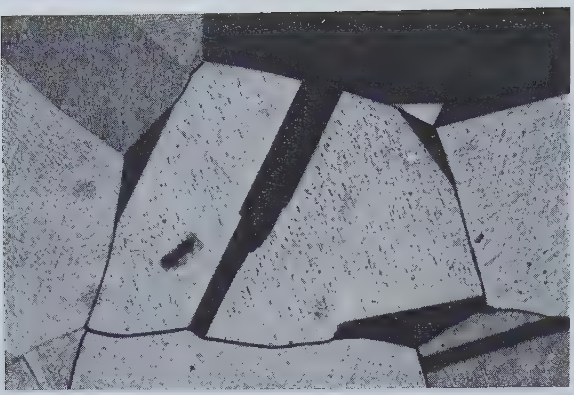

Fig. 5—Alpha brass. X50.

Three twins of different families forming on three corners of a grain.

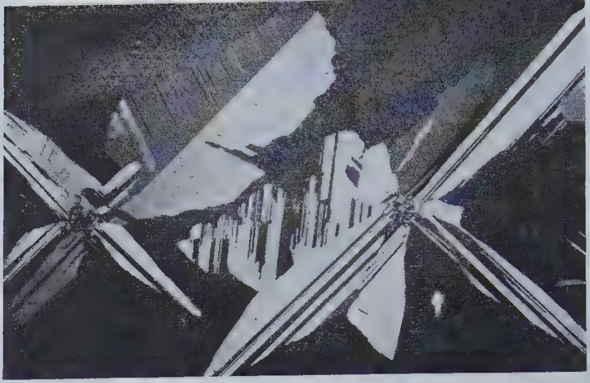

Fig. 6—Grains growing by secondary recrystallization around two indentations in cube-texture copper. X3.

Rolling direction horizontal. Grains growing at 45° twin on octahedral plane held in common with matrix, and occasionally on one other plane. Grains growing parallel to rolling direction twin on a third possible plane.

twins are narrow because the migrating boundaries have met frequent discontinuities, many of which may well be twin faults. The twins that result from the recrystallization of less heavily cold-worked metal are wider because the matrix being consumed is more homogeneous, and thus the growth accidents necessary for the formation of annealing twins are less likely to occur.

In a completely recrystallized metal, twin faults are presumably absent, and the chief discontinuities encountered are grain boundaries. From time to time during its growth, a grain finds itself consuming grains of different orientation. The average distance of migration of a boundary before it meets a grain of new orientation is thus a function of the grain size; the finer the grain size the more frequently will the twinning act occur, and the narrower will be the annealing twins. Thus one would expect to find, as he does, that the twins are broader in coarse-grained specimens.

These observations show that broad twins result from the formation of annealing twins in completely recrystallized metal in which twin faults are presumably absent.[4] They further indicate that a twin fault cannot simply grow to become an annealing twin, since coherent twin boundaries cannot migrate to a new parallel position. The function of a twin fault must be to nucleate a twin of the growing orientation; after this twin has grown to visible size, a second twinning act, possibly at another parallel twin fault, may terminate it to give a parallel-sided twin.

Influence of the Direction of Growth of the Grain

According to the growth-accident hypothesis, twins are formed when atoms deposited from the grain being consumed fall into the twin set of positions on an advancing octahedral plane. This implies that the accident can occur only when the grain boundary approximates an octahedral plane of the growing grain. Thus one would expect that the twinning set which is selected should depend upon the orientation of the migrating grain boundary. A given grain growing in different directions will expose boundaries having different orientations, thus the twinning plane selected should be one which is approximately perpendicular to the direction of grain growth.

In ordinary grain growth it is difficult to determine the direction in which a grain is growing. Cook and Richards,[9] however, have shown that acicular grains will grow around an indentation in cube-texture copper,† and in this case the direction of growth is known. An example is shown in fig. 6. The rolling direction is horizontal, and grains are seen growing both at 45° and parallel to the rolling direction. All the new grains have an octahedral pole in common with the cube-texture matrix and the orientation relationship is the one described by Bowles and Boas,[10] a rotation of approximately 30° about the common (111) pole.

The twins whose traces are parallel to the length of the grains at 45° to the rolling direction apparently formed during the sidewise growth of these grains, since the long side of the grains are the only ones that could be nearly parallel to the composition plane in question.

A cross-section through one of these needle-like grains (fig. 7) shows that the advancing grain front is remarkably straight and quite accurately parallel to the (111) composition plane of the twins in question. Growth is proceeding toward the left, and in the recrystallized part of the grain, the trace of one of the twin bands may be seen. The boundary between the recrystallized and unrecrystallized part is practically straight and parallel to the twin boundaries already formed.

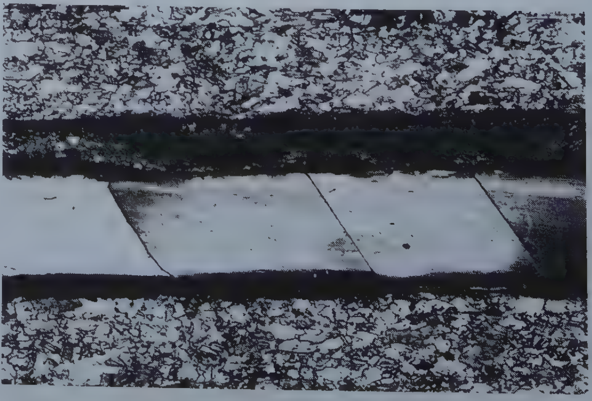

Fig. 7—Cross-section through acicular grain growing at 45° in cube-texture copper.

Growth is proceeding to the left, and the boundary between the unrecrystallized and recrystallized portion is parallel to the twin boundaries on the right.

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† Miss Anna M. Turkalo at the Knolls Atomic Power Laboratory has shown that this phenomenon does not occur in highly perfect cube textures, but only in those which have a sufficient scatter of orientation.

Other families of twins may be found in addition to those whose traces lie at 45° to the rolling direction and which have composition planes parallel to octahedral planes of the matrix. The feather-like grain growing at 45°, which is half black and half white, shows twinning in the black half, on a second twinning plane, which occurred during the longitudinal growth of the grain. The grain growing parallel to the rolling direction shows repeated twinning on yet a third twinning plane, but although these twinning planes are not parallel to octahedral planes in the matrix, their traces in the plane of polish are approximately perpendicular to the direction of growth.

It thus appears that the twinning plane selected is one which is approximately parallel to the advancing grain boundary at the time and place where the twin-producing accident occurs. It remains obscure why grains which have very similar orientations sometimes show twinning of two types, as the feather-like grain, and sometimes only of one type, as do the majority of the grains growing at 45°.

Conclusions and Discussion

From the above observations and arguments it can be concluded that at least three conditions must be fulfilled for an annealing twin to form:

1. The advancing grain boundary must correspond approximately to an octahedral plane of the growing grain at the point where the twinning accident occurs.
2. The boundary must encounter some kind of a discontinuity which will induce a twinning accident.
3. The twinned orientation must be more favorably oriented, as regards ability to grow for example, if it is to be propagated for an important distance.

Annealing twins may form whenever a grain boundary migrates if the above conditions are fulfilled, and not only during recrystallization. Twin faults in the matrix undoubtedly are one type of discontinuity which can lead to twinning. Other types must also exist, however, because twin faults could nucleate only one family of annealing twins in a given grain, while several families are frequently observed.

Octahedral twin boundaries cannot migrate laterally, thus no twin can grow in width unless one face coincides with a grain boundary. This must apply to the growth of twin faults to microscopically resolvable size as well as to the increase in width of microscopically resolvable annealing twins. Thus the appearance of broad twins after grain growth indicates that new twins have been formed during grain growth, and this is confirmed by direct observation. The fact that one observes broader annealing twins in coarse-grained than in fine-grained material leads one to associate one of the discontinuities which can cause twinning during grain growth with grain boundaries.

It is not sufficient that a migrating grain boundary meet a discontinuity to form an annealing twin, it is also necessary that the boundary approximate a (111) plane of the growing grain. Thus there will be relatively few faces on a growing grain which will meet this condition, and it is not surprising that many grains show only one or two families of twins.

There are things which remain unexplained about annealing twins. The above is essentially a crystallographic argument; thus it cannot explain the fact that the intensity of twinning varies from alloy to alloy. Neither does it explain the fact that the number of twins per grain remains approximately constant during grain growth, and that the number is somewhat smaller than the number which appeared at the time of recrystallization. Possibly the explanation is the one offered by Hibbard and coworkers,[8] that the twin-bearing grains are preferentially consumed during grain growth, but there is no obvious mechanism for this, and other factors must also contribute. In addition to the mechanisms for twin broadening presented in figs. *3a* and *3b*, the type illustrated in fig. 3c is also possible; this is essentially a coalescence mechanism, and requires only that the two twins which coalesce be continuous at some point. There is occasional evidence that such coalescence does occur, for example in fig. 4, in the twin just to the right of the center of the field. The driving force for this coalescence is the diminution in the area of the coherent interface, and it should be possible for the incoherent interface to migrate past inclusions just as a grain boundary does. For this mechanism to operate, the noncoherent end of a twin must become detached from a grain boundary. In freshly recrystallized metal, many of the twins are already detached, thus the marked decrease in number of twins per grain observed by Hibbard and coworkers[8] in the very early stages of grain growth may result from this cause. Burke and Shiau[12] showed also that deformations too slight to cause recrystallization resulted in the appearance of many detached twins; presumably because of the presence of distortion it is energetically possible to form the additional interface, but it is not clear that twins could be detached and disappear in this way during normal grain growth.

Acknowledgment

The author would like to thank J. B. Hess, C. S. Barrett, and C. S. Smith for helpful discussions during the development of the arguments presented in this paper. He would also like to point out that Robert Fullman of the General Electric Research Laboratory has been independently working on this problem, and has been able to explain many of the questions unanswered in this paper.

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Transformation Characteristics of a Lithium-Magnesium Alloy

by C. S. Barrett and D. F. Clifton

The martensite-type transformation curves for a lithium-magnesium alloy were investigated in detail by X-ray spectrometer methods. Critical temperatures for formation and decomposition of the low-temperature phase were determined, and the influence of previous thermal and mechanical history investigated.

THE transformation that occurs in lithium and its solid solutions containing magnesium[1, 2] is similar in many respects to other diffusionless transformations of the martensitic type. This general similarity makes it desirable to investigate the transformation curves in detail. The current interest in the phenomenon of stabilization in martensitic transformations has created a need for a careful appraisal of possible stabilization effects in both cooling and heating transformations in lithium alloys. The effect of prior heat treatment on the temperature at which transformation begins and the effect of various temperature cycles in partially transformed alloys also merit attention. Limited data on some of these features were presented previously,[1] but the present studies have been made with improved apparatus, in which erratic fluctuations were smaller than in the earlier work, and include many independent determinations of certain critical observations.

Material and Methods

Geiger counter X-ray spectrometers were used: a Norelco instrument, original model, and a General Electric XRD-3. The low-temperature specimen holder has been described elsewhere.[3] Specimens 10 mm in diam and 1.5 mm thick were held in firm contact with a copper block which was attached to the lower end of a stainless steel tube that extended up to a reservoir of liquid nitrogen. A heating coil on the tube permitted a controlled temperature gradient along the tube, so that desired temperatures and rates of heating and cooling could be obtained by controlling the heating current. The specimen was surrounded by an atmosphere of evaporated nitrogen in an insulated chamber having double cellophane windows. The temperature of the specimen was read by a thermocouple imbedded in it close to the irradiated area; the specimen could be held at constant temperature within 1°C for long periods.

The body-centered cubic 200 reflection near $\theta = 26°$ was used as the index of the amount of b.c.c. material present; occasional checks were made using the most suitable line of the low-temperature phase, the close-packed hexagonal 110 line near $\theta = 29°$. Copper radiation was used throughout. A continuous record was made of the reflected intensities on a strip chart recorder, both when the peak intensity of a line was being followed and when the lines were being scanned at constant temperature. On the continuous recordings of peak intensity, periodic checks were made on the background intensity between the lines, and on the setting of the spectrometer for maximum intensity.

The lithium-base solid solution containing 12.4 atomic pct Mg (33.3 wt pct) that had been used previously[1] was chosen, as it had a transformation range at relatively high temperatures, so as to permit wide temperature cycling within the range. Just prior to use a pellet was cut from the ingot,

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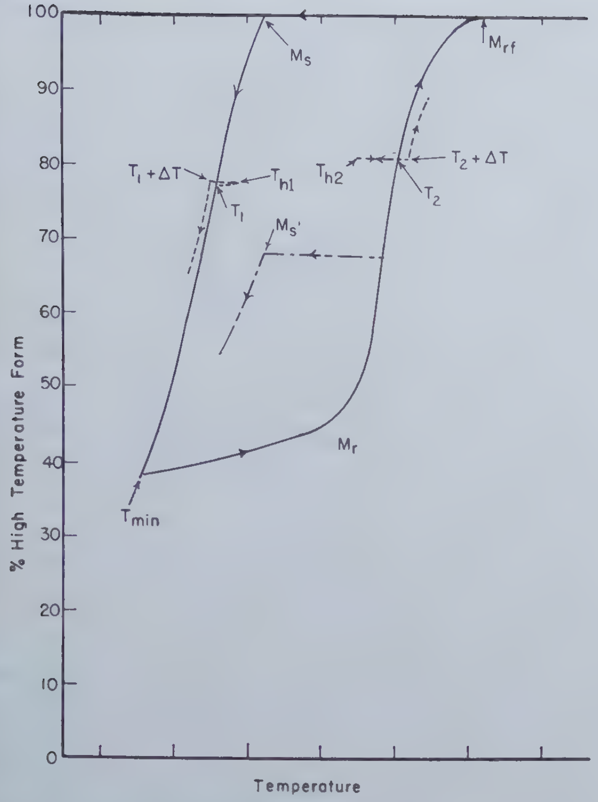

Fig. 1—Typical transformation curve showing nomenclature used and temperature cycles studied.

flattened 70 pct at room temperature, and annealed 15 min at room temperature to insure a fine-grained recrystallized starting material. That this treatment was suitable was checked by a Laue photograph. If a sample was to be used on subsequent experiments, it was kept under liquid nitrogen in the interval to prevent oxidation and grain growth.

Nomenclature

The nomenclature of fig. 1 will be used in presenting the data. On cooling from the annealing temperature the specimen begins to transform at the temperature M_s; cooling may be interrupted at T_1 and the specimen raised to T_{h1} where it is held for a specified time; on cooling again it is found that a change in slope occurs at $T_1 + \Delta T$. A negative value for ΔT would imply that stabilization of the high-temperature phase had occurred during holding at T_{h1}. After cooling to the minimum temperature T_{min}, heating to M_r seems invariably to be accompanied by a slight rise in the percent of b.c.c.; then at M_r a rapid reversion to b.c.c. begins but slows again before becoming complete when the temperature is raised to M_{rf}. If the heating is interrupted between M_r and M_{rf} and the specimen is cooled, transformation to the low-temperature form begins at M_s', a temperature that is always found to be somewhat higher than M_s; if the heating is interrupted at T_2 and the specimen temperature is lowered to a temperature T_{h2} that is above M_s', held here, and raised again to T_2, there is no change in the relative amounts of the two phases present as a result of this cycle. If holding at T_{h2} resulted in stabilization of the low-temperature phase, it would be necessary to raise the temperature to $T_2 + \Delta T$ to cause the reversion to the high-temperature phase to begin again.

Table I. Effect of Annealing Temperature on M_s of Cold Worked Li-12.4 Atomic Pct Mg

	Annealing		M_s
	Time	Temp (°K)	
A*	10 min	245	95
	40 min	220	94
	16 min	260	107
	15 min	263	103
	1 hr	263	105
	2 hr	296	115
B*	15 min	200	105
	15 min	258	113
	15 min	290	118
	150 min	293	120
	17 hr	293	117

* Prior treatment: A, reduced 75 pct in thickness at 77°K;
B, reduced 60 pct at 200°K.

Results

Approximate percentages of the high-temperature (b.c.c.) phase were computed as follows. The peak intensity of the b.c.c. 200 line at a temperature just above M_s was taken as the intensity representing 100 pct b.c.c. at the beginning of the run. The corresponding intensity, when the sample had been cooled and then heated until it just returned completely to the b.c.c. form, was taken as the intensity for 100 pct b.c.c. at the end of the run. It was not uncommon for this final intensity to be about 80 pct of the intensity just before transformation in the first run of a series, but later cycles usually reduced the discrepancy, sometimes to negligible values. The adjustment for intermediate points on the curve was made by arbitrarily assuming that the loss of intensity occurred during cooling and was proportional to the amount of the low-temperature phase that had formed, an assumption based on the idea that strains accompanying the transformation lowered the peak intensity of the b.c.c. line on cooling and that the strains were not altered on heating up to the temperature of complete reversion.* Conclusions were drawn from the data with due recognition of the uncertainty in the computation of percentages from the intensity data.

The shape of the transformation curve on cooling is typical of martensite-type transformations in that with a constant rate of cooling the transformation starts slowly, then accelerates into a range where the amount transformed varies approximately linearly with temperature, and then decelerates. The gradual starting of the transformation when less than 5 pct was transformed made it advisable to determine all M_s values by extrapolating the nearly linear part of the curve back to zero percent transformed. The abruptness of the start of the transformation varied considerably in the different experiments, presumably due to variations in the size, perfection, or surroundings of the individual grains that were first to transform.† M_s itself varied from specimen to specimen, with an average value near 125°K, but was satisfactorily reproducible in a given specimen. Confirming earlier experiments,[1] there was no significant dependence of M_s on cooling

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* Laue photographs and Debye photographs give ample evidence of strains introduced on cooling; however, much of the blurring of the reflections disappears again on heating, so it cannot be claimed that the above scheme of adjustment is exact. A different adjustment would be needed if an alteration of the preferred orientation in the sample occurred during the process, but Laue photographs failed to disclose appreciable orientation changes. The effect of the temperature factor on intensities was judged to be minor.

† J. S. Bowles has noted in experiments in this laboratory that an oil film on the surface of a thin sample of lithium can cause a depression of M_s by many degrees.

Table II. Interrupted Cooling Data for Six Specimens Li-12.4 Atomic Pct Mg

T_1(°K)	T_{h1}(°K)	Time at T_{h1} (min)	ΔT
122	124	20	−½°
138	139	30	−2
109	111	30	0
124.5	126	30	−1
131	133	30	−½
109.5	111.5	92	−1
108.5	114	1080	−½
115	116	35	0
109	110	24	0
121	123	30	0
120	121	6	0
117	155*	1	0
117	149*	19	0
111	146*	12	−2
		Weighted Mean	−0.33 ±0.2°

* T_{h1} above M_s'

rate; in the present tests the rates varied from 1° to about 30° per min.

The previous conclusion[1] that M_s is lowered by cold working a specimen prior to cooling was confirmed, and since it was essential in the current studies to know what annealing treatments would remove the effects of this cold work, a number of experiments were conducted of the type listed in table I, in which a series of M_s values were determined by cooling to 80°K after each of a succession of annealing treatments at temperatures above M_{rf}. Annealing for about 15 min at room temperature appeared adequate for removing the effect of cold working. Laue patterns contained sharp spots after room temperature anneals, and judging by the number of spots on the patterns a room temperature anneal of more than 72 hr is needed for appreciable grain growth to occur.

The data of table I and similar experiments indicate that M_s for a cold-worked specimen is raised by annealing in the temperature range 200° to 290°K; a short anneal of 15 min or so in this range appears to be as effective as a longer one, which is strange and would not be expected from the usual time-temperature relations in recrystallization.

The effect on M_s of annealing a fully recrystallized specimen at various temperatures above M_s was investigated. After annealing at 293°K for 1 hr or longer, each specimen was cooled at about 10° per min to about 140°K, then at 5° per min to determine M_s, then the same specimen was annealed at 195° to 210°K for various times up to 44 hr, and M_s was again determined without warming it above the annealing temperature or, except for two tests, removing the specimen from the apparatus. In seven experiments of this kind the effect on M_s varied from a decrease of 6° to an increase of 2°; the average change for the entire series was a decrease of 2° below the M_s for the 293° annealed condition. When the same specimens were annealed again at 293° to 300°K and, following this, the M_s again determined, it was found that this higher temperature anneal tended to raise M_s again to its original value —an average increase of 2° over the previous M_s was found. (Individual experiments in a series of nine varied from a 6° increase to a 1° decrease.) The estimated precision in determining individual M_s values lay between 1° and 2° in each experiment, so the observed trends are barely larger than experimental error.

Table III. Interrupted Heating Data for Li-12.4 Atomic Pct Mg

T_2(°K)	T_{h2}(°K)	Time at T_{h2} (min)	ΔT
174	173	30	0
165	145	30	+2
165	147	30	+1
164.5	164	8	+2
170	169	22	+1
161	159	960	0
152	147	1080	0
		Weighted Mean	0.16 ±0.4

Table II presents the tests for stabilization during cooling. A sample was cooled to T_1, then warmed to T_{h1}, held for a time and then cooled through the temperature $T_1 + \Delta T$ at which transformation is abruptly resumed (fig. 1). Judging by the fluctuations in the recorded counting rate and the change in slope at $T_1 + \Delta T$ the error for each determination of ΔT was estimated; for half of the determinations this was ½° to 1° and for the balance it was 1½° to 2°; the squares of the estimated error for each determination were used in determining the weighted mean ΔT and the standard error for the series. The weighted mean and standard error for the 14 determinations is $\Delta T = -0.33 \pm 0.2$. There was a marked trend for the more precise determinations to give the least indication of stabilization, and there was no consistent trend toward stabilization with longer stabilization anneals or with lower temperature anneals. It is concluded, therefore, that the results indicate no stabilization of the b.c.c. phase by holding either above or below M_s'.

Table III lists corresponding tests for interrupted heating. The estimated error for the last two determinations was ½°, and for the others, 2°; experiments with greater inaccuracy were discarded. The last three lines of table III are for experiments in which the temperature was raised in ½° steps, the others for constant rate heating. The weighed mean and standard error for the determination is $\Delta T = 0.16 \pm 0.4$. No stabilization of the low-temperature form by holding at T_{h2} is indicated, though reversion started abnormally slowly as the temperature was raised above T_2. This abnormally slow rate was observed after the two longest holding times, but the data from the other experiments afford no adequate test of this.

After cooling to T_{min}, heating initiates slow reversion of the h.c.p. phase to b.c.c., even below M_r. This result was obtained both by measurements of the peak heights of the h.c.p. 110 and b.c.c. 200 lines, and by the ratio of the areas of these lines, when scanned at two temperatures, as shown in table IV.

Typical transformation curves are reproduced in fig. 2, with shading to indicate the estimated un-

Table IV. Decomposition of Hexagonal Phase Below M_r as Determined from h.c.p. 110 and b.c.c. 200 Lines

Temp of Measurement °K	M_r Temp	Ratio of Areas under Peaks h.c.p./b.c.c.	Ratio of Peak Heights h.c.p./b.c.c.
81	138	1.00	1.15
127		0.92	1.00
81	160	0.95	1.11
154		0.53	0.68
82	145	1.06	1.11
135		0.73	0.84

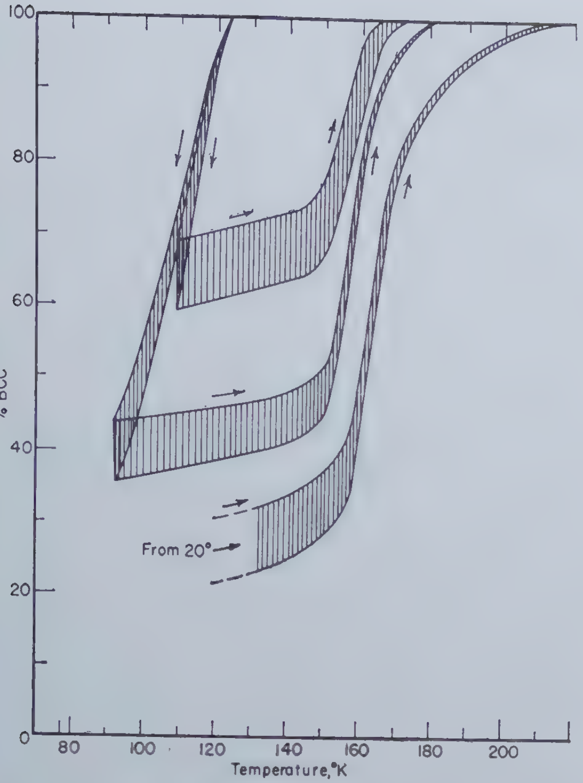

Fig. 2—Transformation curves for Li-12.4 atomic pct Mg.

Shows shift of heating curve to higher temperatures when specimen is cooled to lower minimum temperatures. Shading indicates uncertainties in computation of absolute percentages.

certainty in the percent transformation values. The upper curve was based on the intensity of the b.c.c. 200 reflection, the others on h.c.p. 110. In these and other experiments M_r was always found to lie above M_s. The M_r temperature and the entire curve from M_r to M_{rf} shifts to higher temperatures when T_{min} is decreased.

A specimen behaves in an interesting fashion if heating is stopped at some temperature between M_r and M_{rf} and the specimen is again cooled. Decomposition of the b.c.c. starts at a temperature M_s' that is never lower than M_s, and that becomes increasingly higher than M_s as the amount of the residual h.c.p. phase in the specimen increases. Data from experiments on five specimens are summarized in table V. The exact course of the curve between M_s' and T_{min} is uncertain, but the records clearly indicate a lower slope for this curve than for the initial cooling curve through M_s, as sketched in fig. 1, and the relative amounts of the two phases when T_{min} is reached is approximately the same as on the initial cooling. If cooling from M_s' is continued to lower temperatures, the slope of the curve increases again on passing through the previous T_{min}.

Table V. Effect of Undecomposed h.c.p. on M_s' in Li-12.4 Atomic Pct Mg

Conditions at Start of Cooling		M_s or M_s'
Pct h.c.p.	Temp (°K)	
0	293	129
20	184	129
30	174	133
0	293	120
40	170	121
0	293	139
10	179	140
0	293	123
30	173	123
60	160	133
0	190	126
5	187	128
20	163	136
40	154	138

An understanding of some of these features may be had if the stresses that are generated when a plate of either phase transforms are directed to aid the reverse transformation, and are residual in the specimen when the reverse transformation begins. If, however, the subsequent formation of additional plates on many crystallographic planes has altered the residual stress system into a random one characteristic of cold-worked metal, the effect should be to widen the hysteresis loop of the transformation, as cold working is known to do.[1] It is suggested that stresses favorable to reversion of certain plates to b.c.c. may account for the initial slow rise of the curves in fig. 2, whereas unfavorable, random stresses may account for the shift of the reversion curve to higher temperature as T_{min} is decreased. The fact that M_s' exceeds M_s when appreciable h.c.p. phase is present may also be ascribed to directed residual stresses surrounding crystallites of b.c.c. that have reverted from h.c.p.

Summary

The martensite-type transformation curves for a lithium-magnesium alloy containing 12.4 atomic pct Mg were determined by the X-ray spectrometer method. In fully annealed fine-grained specimens the M_s temperature (which was near 125°K) was slightly lower after annealing near 200°K than after annealing near 300°K, though the amount of the change was of the order of experimental error (2°). Tests for possible stabilization of the b.c.c. phase by annealing in the range 110° to 155°K during an interrupted cooling experiment disclosed no stabilization greater than the estimated error of the best individual experiments (½°). No stabilization of the low-temperature phase (h.c.p.) could be found after annealing at 145° to 173°K during interrupted heating experiments. After cooling below M_s, reversion to b.c.c. began slowly as soon as the temperature began to rise, but rapid reversion began only when a temperature M_r was reached, which was always higher than M_s. M_r and the entire reversion curve above M_r shifted to higher temperatures as the previous minimum temperature was decreased. When reversion was interrupted and the specimen again cooled, decomposition of the b.c.c. began at a temperature M_s', which lay a few degrees above M_s, being higher the greater the percent h.c.p. in the specimen; the rate of transformation with falling temperature below M_s' was less than that for the original cooling through M_s.

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Discussion — Iron and Steel Division*

New York Meeting, February 1950

The Tin-Fusion Method for the Determination of Hydrogen in Steel (paper by D. J. Carney, J. Chipman, and N. J. Grant. *Journal of Metals,* Feb. 1950, TP 2801C) 1333

The Sampling and Analysis of Liquid Steel for Hydrogen (paper by D. J. Carney, J. Chipman, and N. J. Grant. *Journal of Metals,* Feb. 1950, TP 2807C) 1334

The Mechanism of Sulphur Transfer between Carbon-Saturated Iron and CaO-SiO_2-Al_2O_3 Slags (paper by G. Derge, W. O. Philbrook, and K. M. Goldman. *Journal of Metals,* Sept. 1950, TP 2885C) 1336

Evaluation of pH Measurements with Regard to the Basicity of Metallurgical Slag (paper by C. W. Sherman and N. J. Grant. *Journal of Metals,* Nov. 1949, TP 2715C) 1338

The Manganese Equilibrium Under Simple Oxide Slags (paper by J. Chipman, J. B. Gero, and T. B. Winkler. *Journal of Metals,* Feb. 1950, TP 2776C) 1340

Equilibrium in the Reaction of Hydrogen with Oxygen in Liquid Iron (paper by M. N. Dastur and J. Chipman. *Journal of Metals,* Aug. 1949, TP 2661C) 1341

Optical Temperature Scale and Emissivity of Liquid Iron (paper by M. N. Dastur and N. A. Gokcen. *Journal of Metals,* Oct. 1949, TP 2693C) 1341

The Solubility of Oxygen in Liquid Iron Containing Aluminum (paper by D. C. Hilty and W. Crafts. *Journal of Metals,* Feb. 1950, TP 2805C) 1342

Solubility of Oxygen in Liquid Iron Containing Silicon and Manganese (paper by D. C. Hilty and W. Crafts. *Journal of Metals,* Feb. 1950, TP 2806C) 1346

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The Effect of Carbon on the Activity of Sulphur in Liquid Iron (paper by J. P. Morris and R. C. Buehl. *Journal of Metals,* Feb. 1950, TP 2799C) 1349

Side-blow Converter Process for the Production of Low Nitrogen Steel Ingots (paper by R. R. Webster and H. T. Clark. *Journal of Metals,* May 1950, TP 2839C) 1350

Experimental Operation of a Basic-lined Surface-blown Hearth for Steel Production (paper by C. E. Sims and F. L. Toy. *Journal of Metals,* April 1950, TP 2838C) 1350

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* TP 2957C.

The Tin-Fusion Method for the Determination of Hydrogen in Steel

by D. J. Carney, J. Chipman, and N. J. Grant

DISCUSSION, G. Derge presiding

G. A. Moore—The tin-fusion method has been a very favorable possibility for many years. The authors apparently have settled the question that delayed the method for a long time by showing that no hydrogen is absorbed in the tin. This, of course, is very important.

I want to make a few remarks concerning the absolute accuracy of analysis, which must be the final basis for deciding among the various methods. From the figures in the paper, there seems to be some remaining slight discrepancy on the actual amount of hydrogen present in various samples which may be presumed essentially identical. (This is of the order of the precision of individual analyses but appears in averaged results.)

From the analyst's viewpoint, the tally of hydrogen content can be regarded as occurring in three portions. First is a large portion which comes off easily and automatically during sample storage and later on heating in the apparatus. This is fairly easily analyzed. Second is an item which may be either positive or negative in the tally sheet. In warm or hot evolution, this is a portion which, in practice, can never be re-

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moved but which can be calculated with some accuracy. In the fusion methods, we usually tend to get a little too much hydrogen and we have to calculate how much to subtract as the "blank." The accuracy of these calculations may be about the same. Finally, there probably is a little bit more, which can not be accurately estimated except by experience. Dr. Derge always found, I believe, about one hundredth of a volume more by his vacuum fusion than we found by hot extraction. I believe the present work indicates a discrepancy of the same amount.

I had thought that this portion should be accounted for by deciding how you wish to count water. There is certainly a little bit of water, varying with temperature, in every sample. Vacuum fusion tends to convert this to hydrogen and include it in the result, while hot extraction, I think, ignores a good portion of it. I would consider this settled, except that I wish to ask the authors one question regarding the palladium tube used to introduce hydrogen. I suppose this is cut off from the system during analysis, but if not, and if it remains connected in any of the other systems, it is a possible source of the discrepancy which is worrying us. It has been clearly shown that this valve does not always close completely, so that while there is no loss of hydrogen from the supply, there may be a small evolution from the tube into apparatus.

It is pleasing that, in spite of small discrepancies, the authors obtain, by a third essentially independent method, results that are in good agreement with those of the two methods previously found reliable. They remarked on the absence of a standard sample, and I would like to suggest that there is a usable standard which we tried at one time,[11] which is the inclusion of a little lead formate within a steel specimen that previously has been degassed by every known method. The amount of hydrogen in a weighable portion of lead formate is very small.

G. Derge—From my own observations I think the biggest single advantage of this tin fusion has to do with the fact that the gas is largely hydrogen and the apparent improvement in the catalyst efficiency that results. That is the outstanding difficulty that we have in the conventional vacuum fusion. There seems to be very little to choose between the actual results obtained.

D. J. Carney (authors' reply)—Regarding Dr. Moore's questions, one was the possibility of hydrogen coming off the palladium tube after the admission of the hydrogen and the circulation of the gases. We ran a check early in the morning after admitting the hydrogen through the palladium tube. When we checked evolution of hydrogen from the analytical portion of the apparatus, we never found any hydrogen from the palladium tube. We did not check the evolution within an hour after admitting the hydrogen and circulating it, because normally we were still blanking out at that time, but we did not encounter the trouble later in the day. Quite a few checks were made to see whether there was any hydrogen from the analytical portion of the apparatus. In fact, we ran approximately eight blanks a day. Almost every hour another blank was run just to be very sure what it was.

In answer to the other question on the standard samples, we did not consider that possibility. It sounds very interesting. However, is the amount of hydrogen in this lead formate known accurately?

G. A. Moore—There are two hydrogen atoms per molecule of lead formate, that is about one part hydrogen in about 150 parts of the formate. The chemical is obtainable pure and dry.

D. J. Carney—That sounds interesting. Perhaps some use can be made of this.

G. Derge—One thing that has always worried me about this lead formate standard sample is that the hydrogen is not combined in the same way that it is in the steel sample. It is certainly liberated from the formate at a very low temperature and may not become dissolved in the iron. We know enough about the behavior of hydrogen and steel to know that it is tricky, so I would worry about it under these circumstances, although the formate certainly has its advantages in that it is a very convenient form for weighing.

The Sampling and Analysis of Liquid Steel for Hydrogen

by D. J. Carney, J. Chipman, and N. J. Grant

DISCUSSION, G. Derge presiding

G. Derge—With the development of this last weapon, there is not much of a chance for hydrogen. It is certainly a very interesting paper, and it gives us more confidence in sampling liquid steel for hydrogen than we have ever had before. This satisfactory work gives considerable confidence to all of the chilled methods of sampling which should be more or less successful depending upon the degree of chilling obtained.

J. T. MacKenzie—How do you handle a nonmagnetic specimen in that device?

D. J. Carney (authors' reply)—I left that out in going over the analytical procedure. For the 18-8 steel, what was done was to get some iron wire which was degassed. One turn of wire was made around the sample; it was inserted into the analytical apparatus, and that was enough to allow the magnet to pull the sample and drop it in the furnace. Other methods could be devised for this apparatus to do the same thing. This was just a quick method.

C. E. Sims—This method of sampling and analysis is very ingenious, and the results obtained attest to a satisfactory degree of accuracy. It was noted in the paper that the samples are satisfactory only when there is a complete absence of pipe. This should be emphasized, particularly in view of the fact that they are cut off under water.

Some reservations are held in regard to the adequacy of the method of sample storage prior to analysis. Cooling on dry ice undoubtedly slows down the rate of diffusion to a marked degree, and it obviously suffices when the analysis is made within a few hours. All of the samples, except some of high-nickel steels, were analyzed within 12 hr. It is still unknown how long this method would be safe.

In the work at Battelle Institute, it was impracticable always to start analysis within 12 hr for various reasons. Some samples did not reach the laboratory for several days, and some were held as long as a month before analysis. During this period, they were held over mercury, and the gas evolved at room temperature was collected and analyzed. It should be mentioned that both the mercury and the container must be kept very clean.

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In both the methods just described and in the Battelle method, where the molten steel is cast in a copper chill mold, there is a short period of grace during which the sample may be handled without loss of hydrogen. In the latter method, the sample was stored over mercury within 3 min. Some time after 10 min, but seldom later than 15 min, the first small bubble of hydrogen could be seen. After 30 min, there might be as much as ½ ml of hydrogen. The reason for the time lag is that, during freezing of a ferritic steel, the hydrogen is driven from the surface and concentrates toward the center of the specimen, and it takes some time to diffuse back. After about one week, as little as 10 pct or as much as 50 pct of the total contained hydrogen might escape.

It was mentioned that some high-nickel steels, presumably austenitic, were held as long as three days before analysis. Our experience showed that hydrogen does not evolve from austenitic steels, such as 18-8 stainless, at a perceptible rate when held at room temperature. After holding some samples over mercury for as long as a month without any visible evolution, subsequent samples were merely kept in marked envelopes while waiting analysis. These steels usually hold from 2 to 5 times as much hydrogen as typical pearlitic steels.

The results obtained here for commercial steels appear to be of the same degree of magnitude as those obtained by the hot-extraction method. One point of difference noted in the reported analysis of commercial steels was the sharp increase in hydrogen content following the addition of manganese or silicon to the furnace. We always noted a tendency for the hydrogen content to increase whenever the boil was stopped or even slowed down, but no such sharp increase as noted in some of these tests. In Heat No. 9, table VII, for instance, the hydrogen increased from about 2.3 to 5.5 ppm in 7 min after an addition of silicon. In the following heat, there was no change under apparently similar conditions. It does serve, however, to emphasize the fact that deoxidized steels are markedly more susceptible to hydrogen pickup than the same steels before deoxidation.

G. Derge—I would like to add my comment on the advantages of using a quartz tube as an improvement on the conventional Taylor sampler. We have done it for some time in our laboratory in connection with oxygen sampling when we have had very small heats and they would chill up if we immersed the regular Taylor sampler into them. By using that little quartz tube on the end you not only get a better sample but it is much more convenient and easier to handle, and I am glad to know that this has been borne out in the hydrogen work.

Concerning the problem of slow evolution of hydrogen after a heat has become saturated: Are not the refractories a likely source of the gas? It takes about 4 hr to bake the analytical system down to a satisfactory blank in a very good vacuum. It seems reasonable then, that when working on a much larger scale with porous materials which have been intentionally saturated with the gas, it should take a long time to completely eliminate all of the hydrogen.

S. Marshall—With reference to what you said, Dr. Derge, I have another thought about the observed slow evolution of hydrogen. It has been my experience that commercial helium contains hydrocarbons, and I wonder if the authors really had a pure helium atmosphere. Was this possibility also considered in making up the known gas mixtures? For instance, where the gas supposedly contained 5.8 pct hydrogen it could have contained more, with the result that the metal sampling technique may not have been as accurate as the analytical results showed.

J. F. Elliott—I want to add one point on this matter of the deoxidizer. In our laboratory, there has been an extended survey as to oxygen pickup by the tapping stream as metal goes from the furnace into the ladle. This is widely variable from heat to heat, depending upon the turbulence and the fall of the stream. If there is a wide variation in oxygen pickup, certainly there will be some effect caused by moisture in the air, and consequently the moisture content of the air will be a further variable. Perhaps some of the variability noted after the deoxidizer has been added may be attributed to this.

I also am pleased to note the unit of parts per million. It appeals to me.

N. J. Grant (authors' reply)—I would like to express my thanks first of all to everyone for contributing to the discussion.

The first question that Mr. Sims raised concerned the safe storage time for samples which lose hydrogen during storage. Twelve hours was not a maximum time. It happened to be a time that was set as the safe maximum necessary for us to consider in most instances. This was more than adequate when one considers that the total analytical time for any one sample was only 15 min. As a result, we could easily take twice as many samples as others have been able to take, since we were able to analyze many more than twice as many samples during the same period of time; and we found it unnecessary to store samples more than 12 hr. We are not sure how much longer than 12 hr ferritic samples can be kept.

However, on samples which were stored up to 12 hr, we took periodic checks and found that there was no measurable loss of hydrogen over that period of time. There might be a small loss, if the hydrogen were extremely high.

Regarding the remarks on mercury storage, I might add that in a side study using the same equipment we have studied a large number of cathodically charged 1020 steel samples. We tried checking some of these under a mercury column, and I think the most important thing I can say is that out of several dozen samples which were run over that period of time, we did not get a uniform evolution of hydrogen. We found some steel samples with as much as 9 ppm in which the hydrogen was lost rather slowly over a period of 72 hr. We found other samples with as little as 3 and 4 ppm in which the hydrogen was lost at a much more rapid rate. I recall three or four samples in particular which had about 5 ppm in which for the first period of a half hour there was no evolution of hydrogen. We feel that the rates which have been indicated by the mercury storage system are neither accurate nor reproducible.

Regarding the evolution in austenitic steels, I think we concur. We did not run extensive tests on hydrogen evolution out of austenitic steels, but I think we feel the same way, that the evolution is very, very slow and that the samples were probably stable for a long period of time.

Our results show that manganese was seldom effective in bringing about a change in hydrogen content. In one or two instances small jumps were noted, however manganese being a poor deoxidizer had a small effect on the hydrogen content.

Silicon, which is, of course, a much more effective deoxidizer, brought about bigger jumps in the hydrogen content, and in these particular instances we feel that the increase in hydrogen is due to the pickup of hydrogen from water vapor either in the openhearth furnace refractories or in the slag itself. Under those circumstances hydrogen in the slag over a deoxidized bath could certainly account for the hydrogen pickup.

I think that this is the answer to Dr. Derge's question where he suggested a source for hydrogen in the experimental furnace. We think it was water vapor in the refractories that could have been giving us this slow change which resulted in a final value between 1 and 2 ppm of hydrogen.

D. J. Carney—Regarding Mr. Marshall's question, I took a gas sample at the end of the second hour, and there was no hydrogen in the exit gas. I did not analyze per hydrocarbons, however, so that there is that possibility.

The Mechanism of Sulphur Transfer between Carbon-Saturated Iron and CaO-SiO_2-Al_2O_3 Slags

by G. Derge, W. O. Philbrook, and K. M. Goldman

DISCUSSION, J. S. Marsh presiding

T. Rosenqvist—The most interesting point in this paper is the observed transfer of iron into the slag in the initial stage of the desulphurization process, after which the iron again is reduced to the metallic state. The authors interpret this observation as showing that the sulphur enters the slag as an iron-sulphur compound which subsequently is decomposed by the slag.

The present writer has previously suggested the following equation for the desulphurization process:

$$\underline{S} + O^{2-} \rightarrow S^{2-} + O \qquad [1]$$

For *equilibrium* in the blast furnace the oxygen potential is defined by equilibrium with graphite and CO of 1 atm pressure:

$$C + O \rightarrow CO \qquad [2]$$

During the desulphurization process the reactions proceed in the direction of the arrows. If one assumes eq 2 to be significantly slower than eq 1, the transfer of sulphur into the slag, in accordance with eq 1, will build up a *local* oxygen potential at the metal-slag interface very much higher than that corresponding to the value defined by eq 2. This is possible because the equilibrium oxygen potential in eq 1 is high as long as the sulphur content in the slag is low. This oxygen potential will again be able to oxidize some iron:

$$\underline{Fe} + O \rightarrow Fe^{2+} + O^{2-} \qquad [3]$$

and an increase in the iron content of the slag will be observed. Adding up eqs 1 and 3 one obtains:

$$\underline{S} + \underline{Fe} \rightarrow S^{2-} + Fe^{2+}$$

The net effect is thus in harmony with the experimental observation but is obtained without assuming any close ties between the sulphur and iron atoms during the process.

Furthermore, it follows from eqs 1 and 2 that when the sulphur content in the slag increases, and equilibrium with C and CO is finally approached, the local oxygen potential at the metal-slag interface will decrease, and the iron in the slag will be reduced back into its metallic state.

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C. E. Sims—The data and conclusions presented in this paper are thoroughly convincing in establishing the mechanism of sulphur transfer from iron to slag as in a blast furnace. The evolution of gaseous CO in step 3 of the reactions given on p. 1112 makes the process virtually irreversible. Assuming that the process is similar in slag-metal systems other than in the blast furnace, it is readily seen why free CaO and reducing conditions so greatly favor desulphurization. On the other hand, the very effective desulphurization obtained in oxidizing slags when strongly basic, must be attributed to the relatively high stability of CaS as compared to FeS.

The ease and simplicity with which the reactions of classic chemistry agree with the experimental data and explain the mechanism is noteworthy. The concept of molecules of FeS, soluble in both phases (metallic iron is not soluble in the slag), migrating from the iron to the slag and there reacting with CaO, which is soluble only in the slag phase, is clear and uncomplicated. This is likewise true for step 3. Those who would deny the existence of molecules or molecular-type combinations in liquid iron, must strain to provide a mechanism so lucid. In the absence of molecules, the Fe and S exhibit a remarkable collusion.

L. S. Darken—The investigation and interpretation of rate phenomena in the range of steelmaking temperatures is a difficult task. Most of the laboratory investigations of steelmaking reactions have been concerned with equilibrium. Having determined the equilibrium, our attention naturally focuses next on the mechanism and rate of approach to equilibrium. The authors seem to have contributed substantially to our understanding of these factors for the case of sulphur transfer.

I should like to ask the authors whether they consider that the sulphur transfer reaction is diffusion controlled as many high-temperature reactions seem to be. If so, it would seem reasonable to suppose that the slow diffusion step of the process is the transfer across a pseudo-static layer or film similar to that considered in heat flow problems. As the diffusivity and fluidity are smaller for the slag than for the metal, it may tentatively be assumed that the sulphur gradient exists in a thin layer in the slag adjacent to the slag-metal interface and that the metal and the main mass of slag are each maintained uniform by convection. On this basis the amount of sulphur transferred across unit area per unit time is $D\,\rho\,(\Delta S\%)/100\ \Delta 1$, where D is the diffusivity, ρ the density, $(\Delta S\%)$ the difference in percent sulphur on the two sides of the layer, and $\Delta 1$ is the layer thickness. At the beginning of the experiment the main body of the slag and hence one side of the layer contains no sulphur; therefore $(\Delta S\%)$ may be replaced by $(S\%)$, the sulphur content of the slag at the slag-metal interface, which in turn is equal to $L[S\%]$ where $[S\%]$ is the sulphur content of the metal and L is the distribution coefficient. The rate of transfer thus becomes $D\rho L[S\%]/100\ \Delta 1$, which the authors designate $K[S\%]$. Equating these two quantities and setting $D = 10^{-6}$ cm^2 per sec, $\rho = 3$ g per cm^3, $L = 40$, and $K = 10^{-4}$ g cm^{-2} sec^{-1}, it is found that $\Delta 1$, the film thickness, is about 0.01 cm—a value of the order of magnitude of that found in heat transfer problems in liquids. The uncertainty of the numerical values used leaves much to be desired, but at least it can be said that this calculation tends to support the proposed model involving diffusion through a film.

Although this does not seem to affect the general argument, I should like to call attention to the fact that the diffusivity[3] of sulphur in hot metal is found (on conversion of units) to be about 10^{-4} cm^2 per sec rather than 10^{-3} cm^2 per sec as stated by the authors.

The three equations written by the authors to express the steps in the overall process of sulphur transfer may alternatively be written ionically as only two

$$\underline{Fe} + \underline{S} = Fe^{++} + S^{--} \qquad [4]$$

$$\underline{Fe^{++}} + O^{--} + C_{\text{(graphite or metal)}} = CO_{\text{(gas)}} + Fe \qquad [5]$$

where the underscore is used to designate the metallic phase; ionic species are slag constituents. After the authors have so neatly demonstrated that iron and sulphur transfer together (at least initially), this fact seems almost self evident; from eq 4 it is seen that if sulphur acquires a negative charge during transfer then something else (iron) must simultaneously be transferred to preserve electric neutrality.

The relative slowness of reaction 5 as compared to 4 is not difficult to understand. This reaction 5 involves a minimum of three phases (metal, slag, and gas) which must be present simultaneously. In general, three material bodies can have only a line in common. If gas bubbles are not nucleated (and all evidence indicates this to be difficult), then this reaction can proceed only on the circular ring where the slag-metal interface is in contact with the pores of the graphite crucible, or by nucleation of iron droplets. This reasoning also indicates that mere increase of the extent of the slag-metal interface does not promote reaction 5—a fact observed in other studies.

In spite of the excellent work reported in this paper, there remains the possibility that the experimental conditions may differ so much from those in blast furnace operation that direct application may not be as fruitful as hoped. The experimental sulphur contents (in the metal) are very much higher than those encountered in blast furnace practice—high enough to approach saturation with iron sulphide. The iron content of the slag is also much higher than in practice. We have been doing some work on the remelting of blast furnace iron and slag. These are remelted in a small graphite crucible—2 in. long, ¾ in. OD—without stirring. We were somewhat surprised to find that the sulphur in the metal dropped (at 1500°C) from 0.027 to 0.010 pct in 2 hr and thereafter did not change in times approaching 70 hr. Similarly at 1400° and 1600°C, we found an initial rapid drop and no significant subsequent change in sulphur content. This is difficult to reconcile with the results of the present paper and with other results. It does seem to indicate a possibility of some difference in mechanism under different conditions. Although the nature of the difference is not obvious, a few possibilities come to mind: (1) Perhaps the slow diffusion stage may be in a thin layer of slag (as suggested above) in one case but in a similar thin layer of metal in the other; (2) although reaction 5 may be slow there are alternative reactions if we are not restricted to a simple system. For example, silicon or manganese could replace carbon as a reducing agent—in which case the gas phase is not a prerequisite. In such case the amount of silicon or manganese would have to be larger (presumably much larger) than that required for this reaction—this condition normally prevails in blast furnace practice but not in the present experiments.

I would like to ask the authors whether they have any evidence or opinion as to whether their proposed mechanism, which seems to fit the initial stage of sulphur removal, is also applicable to the later stage when the sulphur is considerably lower.

J. E. Stukel—During my association with Carnegie Institute of Technology, a number of experiments, suggested by Dr. Derge, were carried out to determine the effect of an electric current on the rate of sulphur transfer. Using CaO-Al_2O_3-SiO_2 slags and carbon-saturated iron containing sulphur, a direct current was passed through the system perpendicular to the slag-metal interface. No effect was observed on the rate of sulphur transfer from the metal to the slag despite the changes in voltage, current density, and current direction. These results seem to substantiate the conclusions reached by the authors in the present paper.

E. Smith—Most of these experiments concern the transfer of iron saturated with sulphur to the slag, and I wonder sometimes whether we are on sound ground in working that way, because in the iron-reducing industry, where they do not melt the iron, there are some rather unusual things to think about.

I am quoting here from the writings of Eketorp on Höganas iron, from the 1945 record. It is available in the British Iron and Steel Institute's translation. I have had two or three discussions with Eketorp about it, but he shows Höganas iron is 97.2 pct iron—94 pct of the metallic with 0.009 sulphur in it. Now, it is true he started out with an 0.005 sulphur ore, but, under certain circumstances, if you do not melt this iron, it remains very, very low in sulphur, and John Whiting's figures in the 1938 paper of the American Iron and Steel Institute, on the furnaces that he and his men dug out at Alan Wood, show the sulphur in the iron—that is, the metallic portions—to be very much lower than is generally the case now. Dr. Darken's comment about what the reaction rates would be in low sulphur is worth while thinking about. After looking at Höganas figures, D. E. Babcock and I began wishing for the first time we would have a catastrophe on a blast furnace so we could get a chance to see some of this stuff in place. At Youngstown, about a year ago, we had a very bad hearth break-out that caused enough damage to stop the furnace. Instead of the usual dig-out through the tuyeres, with one side out of the furnace open, we had an opportunity to go in and get some of the stuff that was there, and I dug out one lump of lime that was 8 ft above tuyere level and 4 ft in from bosh wall. Even though the furnace had been soaked out, the lump still had a tremendous concentration of sulphur in the outside bark. I wonder if that blast furnace is not acting like Eketorp's Höganas reduction.

The figures of John Whiting's are not 1 pct sulphur iron; they are 0.3 and 0.4 sulphur, and even lower, and Eketorp was shipping lots of iron under 0.010 sulphur.

I wonder in some cases if we do not resulphurize the iron as we come to the hearth and desulphurize it as it stays there, but I do not like to see you calculate it entirely on an iron-sulphide equilibrium. On some of the figures we get I am prepared to say I do not know whether it is the same iron in the same slag, but the kind of iron that a blast furnace will make occasionally is something to be hoped for.

I wonder if anyone had a chance to dig a lump of lime out in a place not soaked with water. The lump we had has a cored effect, with a tremendous absorption of sulphur; and surely we did not have all of it because of the water that had been on the furnace. If anybody should have a lump of lime from one of those furnaces and has the composition, I would appreciate knowing what it is, and if anybody has figures from Höganas on what the coal and lime is on the Swedish reduction, I would appreciate very much having it, because I would still like to know what is going in that does not go into the iron.

B. M. Larsen—For the sake of an ultimate understanding of the exact mechanism of this process I would merely like to mention here certain possibilities to be kept in mind. Recent data tend to indicate that the blast furnace does not quite reach equilibrium in sulphur removal, so the most interesting possibility is that of some limiting step which makes it difficult to approach the true equilibrium.

Is it possible that there is enough carbon in solution in blast furnace slag (as in the carbide slag in the electric furnace) to react with FeO by a homogeneous reaction? At any rate, whether by this mechanism or by a surface reaction with coke surfaces, perhaps the difficulty is that of evolving CO bubbles. Perhaps the main pool of slag and metal is in effect in equilibrium with several atmospheres pressure because of reluctance to form bubbles of CO, once the slag and metal have dropped into the pool on the hearth?

As regards the movement of most of the sulphur in a commercial blast furnace, it seems probable that most of the sulphur comes by liberation from the coke by the combustion at the tuyeres, and much of this sulphur must start upward in the gas phase. We find, at most, only extremely small traces of sulphur in the top gases, but this is probably due to the fact that the tall shaft and its contents make an extremely efficient trap for sulphur absorption from the gases, with iron oxide, sponge or liquid iron, and lime lumps all reactive toward sulphur compounds.

C. E. Sims—I can report some experiences that confirm the observations of Mr. Smith. Some years ago

I was working on the low-temperature reduction of iron ore by mixing it with coke and heating it to about 1800°F in a rotary kiln. When granulated limestone or burned lime was added to the charge, it absorbed a large part of the sulphur. It seems obvious, therefore, that this also occurs during the reduction stage in a blast furnace. Later, when the lime melts and becomes combined as a silicate, much of this sulphur transfers to the liquid iron.

G. Derge, W. O. Philbrook, and **Kenneth M. Goldman** (authors' reply)—The authors appreciate the suggestive comments which have been made and wish to thank the discussers for their interest. Many of the questions will be resolved by research which is now in progress. The authors would like to indicate their position on a few items.

The ionic reactions proposed by Dr. Darken and by Mr. Rosenqvist are certainly possible alternatives to the mechanism of the authors. However, neither proposal takes complete account of all the reactants involved, and they would both require additional confirmatory evidence to become established as correct. We certainly agree that slag-metal reactions must finally be thought of in ionic terms[10, 17] and welcome the acceptance of this idea, but the experiments at hand do not seem to contribute directly to new knowledge of this type. Experiments of the type reported by Mr. Stukel should be definitive on questions in this field, and we look forward to their completion.

The authors wish to emphasize the position taken in the paper, that the schematic representation of the mechanism we have used is not to be taken literally and only indicates the types of association which probably exist in highly solvated form in both the slag and metal phase. This would be our only comment on the discussion of Mr. Sims.

We agree with Dr. Darken that the concept that the reaction may be diffusion controlled through a thin stagnant film at the interface is a plausible one which is consistent with theories of heat transfer, absorption, and other processes involving fluid on one or both sides of an interface. The question is largely a formal one of method of treating a heterogeneous reaction because evidence of such a film has not been established as it has for some of the processes which have been studied intensively by chemical engineers.

The importance of CO evolution as a rate-controlling process and the difficulty of bubble formation was brought out by Messrs. Sims, Darken, and Larsen. If this is so, the experiments indicate that the slag-metal interface can nucleate CO bubbles, for the rate of sulphur transfer is directly proportional to this factor. It would also appear that in any commercial blast furnace there is ample solid surface available at slag-coke and slag-refractory interfaces so that nucleation should not be difficult.

It is true that these laboratory experiments were made in concentration ranges which were designed to give good analytical data and elucidate the general features of the sulphur reaction. However, we feel that careful consideration of the data gives no indication that the features which have been observed are not operative in a blast furnace. The rate constants of table II, and those reported by Chang and Goldman,[2] apply over a wide range of composition which actually overlaps the values reported for the sulphur in iron in the region of the bosh and tuyeres by Kinney.[18] Similar slag and metal compositions have long been used in laboratory studies, such as those of Joseph,[4] which have been tested by time and found pertinent and useful in interpreting blast furnace operation. The slag compositions are quite comparable with commercial practice. The behavior of the "reacted slag" in the "reverse transfer" experiments of fig. 7 also suggests that the processes are reversible and apply equally well to transfer from slag to metal, even though the evidence in this direction is not complete. It is therefore necessary to produce some pertinent evidence, if the general applicability of the mechanism to blast furnace operations is to be discounted.

As Mr. Larsen has indicated, a relatively small amount of sulphur leaves the blast furnace as top gas. Regardless of the reactions above the tuyeres, the sulphur output is through the slag and metal. Therefore, even if the solid reactions of lime and iron discussed by Mr. Smith occur, as they probably do, the final sulphur content of the iron is largely determined by rates of slag-metal reactions, for it would appear from the work of Hatch and Chipman[1] that equilibrium is seldom realized. The solid reactions in the shaft have been examined by Kinney,[18] who shows that stone which contained only 0.04 pct S as charged analyzed 0.7 pct S above the bosh, accounting for about 25 pct of the total sulphur charged. Kinney also showed that sponge and pelletized iron absorb sulphur from the coke, until they become covered with slag in the bosh region.

In the active continuance of this program, the influence of alloying elements such as silicon and manganese, the quantitative relations of CO evolution, and the relative importance of slag-metal and slag-graphite interfaces are all under study, and other factors will be included as the opportunity arises.

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Evaluation of pH Measurements with Regard to the Basicity of Metallurgical Slag

by C. W. Sherman and N. J. Grant

DISCUSSION, J. S. Marsh presiding

W. O. Philbrook—The authors are to be complimented for a very careful and exhaustive investigation of the pH method and particularly for the thoroughness of their efforts to correlate the pH measurements with the chemical properties of the slags. The extension of the method to blast furnace slags was especially interesting and fruitful.

The modifications of technique required for this work can probably be attributed to the greater extent of hydrolysis of blast furnace slags compared with openhearth slags, as indicated by the propensity of the former to clot upon the addition of water or acids because of the formation of gelatinous silicic acid. It has been well established that there is no "right" value for the pH of a slag, because the values obtained depend upon details of the procedure which are somewhat arbitrary.

The authors have made the interesting discovery that pH readings for both blast furnace and openhearth slags fall on the same correlation line relating pH to millimols of excess CaO, the latter being calculated on the hypothesis of metasilicate compounds in the solid slag. The apparent accuracy of this correlation is perhaps unduly enhanced by the condensed pH scale used in plotting. In figs. 8 and 9, the ordinate scale

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W. O. PHILBROOK, Carnegie Institute of Technology, Pittsburgh, Pa.; W. A. SMITH, J. MONAGHAN, and W. HAY, Clyde Tube Works, Stewarts and Lloyds, Ltd., Coatbridge, Scotland; G. HATCH, Armour Research Foundation, Chicago, Ill.

ranges from pH 7 to 12, but experimental points fall only in the range from 9 to 12. The practical application of the correlation would be to predict an excess CaO value from a measured pH. Using figs. 8 or 9 for illustration, at pH 10.5, one would predict an average value from the line of excess CaO = 1.2_3 millimols (log millimols = 0.09), but actual experimental points range from 1.0 to 1.5 millimols (log millimols 0 to 0.18). If one draws on fig. 9 a band which includes most of the experimental points, it will be found that for any given pH value, the range of excess CaO values is about ± 25 pct of the average value. It may be noted also that in going from figs. 3 and 4 to fig. 6, the authors have dropped about a dozen points, including all those of pH less than 9, and in passing from figs. 7 to 8 they have omitted 4 points including all those of pH less than 10. These comments do not in any way deny that a correlation exists, but serve to point out that it is not highly precise—in fact no more precise than the empirical relationships between pH and lime-silica ratio for openhearth slags that have been obtained in the work covered by the first three references of the paper. When it is considered that the hypothetical metasilicate compounds that serve as a basis for the excess CaO calculation seem to have no real significance in relation to the properties of molten openhearth slags, it must be concluded that the present paper has not extended the usefulness of the pH method for the openhearth operator.

For the blast furnace operator, on the other hand, the paper offers a good possibility for a new control tool. It would seem well worth while to attempt a correlation between pH values of flush and cast slags and the sulphur content of the iron cast, due regard being given to the influence of other simultaneous variables. Fig. 12 suggests that a reasonable correlation might be found, but a practical test is needed. Slag pH values might provide a logical basis for short-run changes of blast temperature to compensate for variations in slag composition resulting from nonuniformity of raw materials, or for minimizing swings in sulphur content until burden changes can become effective.

One of the most significant observations in the paper is independent of the pH studies and deserves treatment in a separate report. Fig. 11 represents a new method of interpreting the Hatch and Chipman data on the equilibrium desulphurizing power of blast furnace slags. Fig. 11 presents an exceptionally good correlation—almost phenomenal for process metallurgy data. If the correlation is significant, then an important conclusion regarding the chemistry of desulphurization seems to stem from the method of calculation. In calculating excess CaO, the acids in the slag are first assumed to have been neutralized by the bases on a mol-for-mol basis. Silica and alumina are given equal weight as acids, and magnesia and lime are equally strong bases *in the neutralization of acids.* After the acids have been neutralized, however, only excess CaO is *effective in desulphurization;* and, significantly, it matters not whether the Ca is present in the slag as CaO or CaS. This seems to imply that free Ca (as some ion, atom, or molecule) exerts a mass-action influence on desulphurization. Presumably free MgO is not at all effective in desulphurization, although it is as active as CaO as an acid neutralizer. The influence of manganese is unknown for want of data. This represents a new viewpoint on desulphurization by nonoxidizing slags, and we would like to know whether the authors believe this to be a necessary or reasonable interpretation of their data.

The authors have not at all improved the usefulness of the pH method to openhearth control, but they may have provided a new tool which can be developed to offer some short-range control of sulphur variation in blast furnace iron. Their treatment of the Hatch and Chipman data has suggested a new viewpoint on the chemistry of desulphurization by nonoxidizing slags.

W. A. Smith, J. Monaghan, and W. Hay—The authors are to be congratulated on their very careful work on pH measurements, which has contributed to a further understanding of the meaning of basicity. The evidence that the same relationship exists between the pH of the water extract and the millimols excess CaO for blast furnace and openhearth type slags, extends the range of usefulness of the pH technique and provides support for the assumptions made in calculation of the excess CaO.

That the V-ratio is an inadequate parameter for comparison against pH measurements has been demonstrated by earlier work, though the authors do not quote results over a sufficient range of basicity to enable one to judge if the correlation is any poorer than that reported by the writer or other workers.

The V-ratio cannot be entirely dismissed however in a consideration of slag-water extracts, as is evident from the close relationship which exists between log V-ratio and log specific conductance of the water extract. A further examination of the conductance data by Kerlie[6] showed the relationship between V-ratio and conductance might also be represented by a series of straight lines, passing through zero conductance at about 1 V-ratio, and with breaks at about 2 and 3 V-ratios corresponding approximately to the $2CaO \cdot SiO_2$ and $3CaO \cdot SiO_2$ compositions, the conductance increasing more rapidly with basicity after each break.

This and other evidence suggests CaO to be the main constituent responsible for the conductance effect, the amount leached out by the water being proportional to the excess CaO above that required to form $CaO \cdot SiO_2$, $2CaO, SiO_2$ and $3CaO \cdot SiO_2$, in turn. That only a proportion of the CaO present takes part is evident from the abnormal effect which occurs in the presence of CaO incompletely digested in the slag. Lack of complete analyses prevents calculation of the millimols excess CaO on the slags used for the conductance investigation, but a comparison of specific conductance values with the pH measurements on the slags used by the authors would be of interest and should throw further light on the subject.

No mention is made in the paper of the type of electrode used for the pH measurement. Some difficulty was found by the writers in using a glass electrode at high pH due to attack of the glass and a time lag before a steady reading could be obtained. Even with an alkali resistant glass electrode, considerable care was needed to obtain reproducible results, this being a contributory reason for abandoning pH measurement in favor of conductance. Perhaps the authors could state their experience in this, and the type of electrode they found to be most suitable.

G. Hatch—I should like to discuss fig. 11. For metal samples containing 0.006 pct sulphur or less, the inaccuracies in chemical analyses alone are ± 10 pct, or more. Thus, in the upper portion of the plot shown in fig. 11, it is only natural to expect a scattering of points.

Second, the lower point on this plot is actually not an equilibrium point. This particular run was remelted, and equilibrium was established. The equilibrium distribution ratio for the run is actually 140 and not 100, as indicated in the plot.

Now, undoubtedly there is a correlation between the index of excess lime developed in the paper and the sulphur distribution ratio. The only point I wish to make is that this particular line, in which every point is on the line, actually detracts from the significance of this index, excess lime, as a means of correlating equilibrium sulphur distribution ratios.

C. W. Sherman (authors' reply)—The authors wish to thank the discussers for their comments on the paper. We are especially indebted to Dr. Philbrook for a complete discussion of the work. It might be well to say at this time that we were not attempting to champion the pH method but were trying to examine the method critically in the hope that the results themselves would indicate its degree of usefulness.

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[6] W. L. Kerlie: Discussion. *Journal* Iron and Steel Institute. (1949).

Dr. Philbrook commented on missing a few points on figs. 6 and 9. The points that we left off these two figures were slags of very low basicity and could not be fitted on a log plot conveniently. If they had been included, the majority of the data would have been grouped so closely that the scatter of points would not have been evident.

The summary of the interpretation of the Hatch and Chipman data emphasizes precisely the viewpoint of the authors with regard to the behavior of nonoxidizing slags. Further research is being conducted in an attempt to substantiate this interpretation.

In answer to Dr. Hatch, the straight line relation in fig. 11 would not be as straight had it not been for the very careful work of Dr. Hatch in his original investigation. The heats took 9 or 10 hr to make, and the fact that he stuck with them to the bitter end shows up in this plot. He mentions one heat that had a sulphur ratio of 140 when remelted. Many things can occur when one remelts the slag. The equilibrium conditions might not have been the same. Since the remelted heat had not been completely analyzed, the datum plotted represents the value for the original heat. The authors fail to see how the fine correlation of the data detracts from the significance of the index, excess CaO.

There is one additional point that I would like to explain since I was associated with Dr. Hatch in this work. Sulphurs were analyzed as closely as possible because of the variation in high sulphur ratio at low metal sulphurs. The metals ran as low as 0.004 pct S. An error of 0.0005 pct was significant. It was felt that the combustion method of analysis for sulphur, very carefully employed, would give ± 0.001 pct accuracy. That was the best that could be hoped for. Many of these analyses were made by the writer. When the results were first reported, the writer recommended that in each case the higher sulphur value from duplicate sample be reported. In other words, if 0.0055 and 0.006 were found, 0.006 pct was accepted. If 0.005 and 0.006 were found, 0.006 pct was reported. There were three points in fig. 11 that did not plot exactly right, but going back and checking the data and averaging the original duplicate sulphur analyses made the three values fall right on the line.

In reply to Messrs. Smith, Monaghan and Hay, the same difficulty was experienced with electrodes that they mentioned. However, the glass electrode with its accompanying time lag seemed to give results that were reproducible. The electrode was rechecked after each unknown sample by measuring the pH on buffer solutions of pH 4 and pH 8.

The Manganese Equilibrium Under Simple Oxide Slags

by J. Chipman, J. B. Gero, and T. B. Winkler

DISCUSSION, M. B. Bever presiding

D. C. Hilty—This paper is a useful and timely addition to our store of quantitative data relating to manganese distribution between slag and metal in steelmaking processes. For some time, many of us have suspected that the values of K_{Mn} derived by Körber and Oelsen might be too low, and this paper now appears to confirm that suspicion. Application of the new constant to openhearth data should prove interesting.

The manganese deoxidation curves of fig. 4 agree fairly well with direct measurements of isothermal solubilities of oxygen in liquid iron containing manganese that have recently been made at the Union Carbide and Carbon Research Labs., Inc. According to the solubility data just mentioned, however, the curves for 1550° and 1600°C lie much closer to each other than the authors have indicated. In other words, the solubility measurements suggest that the logarithm of the oxygen solubility is not a linear function of the reciprocal of the absolute temperature, as the authors have assumed for their calculations.

It seems possible that this discrepancy may be due in part to the authors' use of the distribution coefficient, L_O, obtained from Taylor and Chipman's curve for the solubility of oxygen in iron as shown in fig. 2. Taylor and Chipman gave the equation of this curve as

$$\text{Log }\%\text{ O} = \frac{-6320}{T} + 2.734$$

Their data, however, can be fitted equally well by a curve having the equation:

$$\text{Log }\%\text{ O} = 36.350 - \frac{13.23 \times 10^4}{T} + \frac{1.18 \times 10^8}{T^2}$$

Moreover, this curve also fits the authors' oxygen distribution data somewhat better than does the linear curve of Taylor and Chipman. Its use in the derivation of L_O for calculation of the deoxidation curves by the authors' eq 15 causes the effect of temperature on the calculated curves of fig. 4 to agree quite well with the temperature effect that has been observed. An experimental determination of the temperature coefficient of the manganese reaction appears to be desirable.

J. E. Stukel—Because the authors have done such an excellent job, my comments will be confined to additional information.

Very shortly Professor T. L. Joseph and I will publish the results of a study of the reaction between molten manganese and silica. It was found that electrolytic manganese, melted in silica crucibles, reacted with the silica to form a silico-manganese alloy containing 18 pct silicon (1500°C) and a silica saturated $MnO\text{-}SiO_2$ slag. Therefore, the presence of silicon and its oxides in the Fe-Mn-O system will affect the equilibrium.

Carbon is also an important factor. The higher the carbon content of the iron the less ability manganese has to reduce silica. As a matter of interest, recently a study of the manganese equilibrium in carbon saturated iron and blast furnace slags was completed at Carnegie Institute of Technology. As a comparison to the present study, 2 to 5 hr were required to reach equilibrium and temperature was a much more important factor than slag composition in determining the (Mn)/(MnO) ratio. These results will also be published in the near future.

It can be seen, therefore, that the results of this paper cannot be applied directly to openhearth studies without a degree of flexibility.

J. Chipman (authors' reply)—With regard to the effect of silicon on the manganese constant, this effect is, of course, known. Much more data is needed in order to establish it accurately, and I hope we can look forward to having some accurate data on that.

Mr. Hilty suggests that a three-term expression for the Taylor-Chipman solubility of oxygen in liquid iron might fit a little better than the two-term equation. I think that it would be too great a compliment to the precision of the data to employ a three-term equation, and I would still recommend the simple, two-term expression.

D. C. HILTY, Union Carbide and Carbon Research Labs., Niagara Falls, N. Y.; J. E. STUKEL, Youngstown Sheet and Tube Co., Youngstown, Ohio.

Equilibrium in the Reaction of Hydrogen with Oxygen in Liquid Iron

by M. N. Dastur and J. Chipman

DISCUSSION, C. E. Sims presiding

L. S. Darken—It is gratifying to find that, as a result of this careful and painstaking investigation, the discrepancy in the oxygen pressure of oxygen saturated iron (shown in table II as determined from data above and below the melting point, respectively) is now greatly reduced. As pointed out by the authors, however, the remaining discrepancy of 0.13 log unit, or about 25 pct, is real and is greater than either of us would like to admit as error in our data.

The current upward revision of the aluminum deoxidation constant suggests the faint possibility that aluminum from the alumina crucibles used may affect the present results. Although this seems unlikely, I would like to ask the authors if they analyzed for aluminum and, if so, whether any effect of this type is indicated.

N. A. Gokcen—Analysis of some of the similar heats indicated that the aluminum content within the range of oxygen activities of this work is extremely small. Therefore, the present work is not affected at all by any aluminum reduced from the alumina crucibles used in this investigation.

J. Chipman (authors' reply)—I think some day we will find the source of this rather minor discrepancy. If you look back at the old data, instead of 0.13 log units, in 1934, we had about 1.5 log units, and in 1942 we had about 0.6 log units as the discrepancy. The two series of data are certainly converging and we will get to the bottom of this some day if you give us time.

The aluminum in these melts is known to be less than 0.1. How much less I would not venture to say. Mr. Gokcen is working on this same reaction in alumina crucibles at much lower oxygen concentrations where the aluminum will have probably a very important effect. We hope you will hear about this at next year's meeting.

L. S. DARKEN, U. S. Steel Corp. Research Lab., Kearny, N. J.; N. A. GOKCEN, Massachusetts Institute of Technology, Cambridge, Mass.

Optical Temperature Scale and Emissivity of Liquid Iron

by M. N. Dastur and N. A. Gokcen

DISCUSSION, M. Tenenbaum presiding

R. C. Buehl—It would seem to me that for temperature measurements of this nature, where an induction furnace was used which stirred the metal so the top surface was both rounded and wavy, you get a certain amount of reflection of light from the walls of the crucible. Therefore, the emissivity would be a little higher than if, for instance, you were sighting on a stream of metal coming out of the bottom of a ladle, for which case the light reflected from any hot surface is zero. When a resistance furnace is used and temperatures are measured by sighting nearly vertically downward with an optical pyrometer, the effect of light reflected from the crucible walls on the temperature correction can readily be observed. If one sights on the center of the melt, which only reflects light from the cold end of the furnace, then the temperature correction is found to be about 160°C at 1600°C, which gives emissivity for the iron of 0.40. This value is near that reported by most of the more reliable investigations. If one now sights on the outer portion of the iron surface, which is convex and so reflects light from the heated crucible walls, the temperature correction will be reduced to values around 30°C, where the angle from the horizontal is small to values of a few degrees centigrade close to the crucible wall where the angle with respect to the horizontal is quite large. These small temperature differences give high apparent emissivity values of about 0.83 to almost unity. Similarly, if the metal surface is agitated, as for example by bubbling gas into the melt, the temperature correction is again reduced to a low value around 10° to 20°C with apparent emissivity around 0.9. The light reflected from the furnace walls is, therefore, something which must be considered when determining emissivity factors by the method described.

With the induction heating the crucible walls above the melt are cooler than the melt, so the effect of reflected light from the walls would be much smaller than for the extreme case sighted above. However, even if the crucible walls were relatively cold, appreciable light from the melt would be reflected back to the melt by the crucible walls, provided they were rough and light colored.

The authors appear to have made very careful temperature measurements and the temperature corrections obtained by them would certainly be of value in using an optical pyrometer to obtain the temperature of melts in similar furnaces; but their correction values cannot be used for all types of measurements of the temperature of liquid iron with an optical pyrometer, and the emissivity of pure iron calculated from their data might be somewhat above the true value because of radiation reflected from the metal surface.

R. W. Fenn, Jr.—Recently we have had occasion to check optical temperatures against true temperatures for cast iron. However, precautions similar to those of the authors were not taken. Nevertheless, without these precautions deviations of only 50° to 100° were obtained. Possibly this can be accounted for by what Dr. Buehl has just said. The true cast iron temperatures were obtained by using a platinum—platinum-rhodium thermocouple during the operation of the high frequency furnace. I would like to have the authors' opinion on this particular discrepancy.

J. T. MacKenzie—In cast iron, the emissivity of iron oxide occurs at 1375°C. The unfortunate thing is that that is about the temperature at which many castings are poured. Wensel and Roeser showed that very clearly in their work for the American Foundrymen's Association in 1928. You are talking about two different things when you talk about liquid steel and liquid cast iron.

M. N. Dastur and N. A. Gokcen—The disturbances affecting the brightness of liquid iron are numerous. Factors pointed out by Dr. Buehl were considered in the experimental procedure of this work. The use of various kinds and sizes of crucibles as well as different preheater temperatures were found to have no effect on the emissivity of the liquid iron under our experimental setup. However, the authors' temperature correction and emissivity values may be less accurate for a different type of measurement, as already pointed out in this work, because of the presence of atmospheric disturbing factors and the surface condition of the metal, as investigated by Hall.[10, 20]

As regards Mr. Fenn's question on the deviations of his observation in the measurement of cast iron temperatures, we agree with Mr. MacKenzie that the cast iron problem is completely different from pure liquid iron or steel. This, as well as other factors,[10, 20] may explain the discrepancies between the true and observed temperatures.

R. C. BUEHL, U. S. Bureau of Mines, Pittsburgh, Pa.; R. W. FENN, JR., Dow Chemical Co., Midland, Mich.; J. T. MACKENZIE, American Cast Iron Pipe Co., Birmingham, Ala.

The Solubility of Oxygen in Liquid Iron Containing Aluminum

by D. C. Hilty and W. Crafts

DISCUSSION, K. L. Fetters presiding

J. Chipman—It has been my privilege to discuss this work with the authors on several occasions and to observe at first hand the experimental methods employed. I wish, therefore, to emphasize certain points which they have mentioned only briefly with regard to the experimental techniques.

The rotating induction furnace as here employed interposes liquid metal between slag and refractory thus preventing the two nonmetallic parts of the system from reaching equilibrium with one another. It is therefore impossible for the metallic phase to be completely in equilibrium with both the slag and the crucible. The metal also acts as a partially permeable membrane allowing certain components, including oxygen, to diffuse from slag to crucible. This transfer results in building up on the face of the crucible a layer of material whose composition is in part dependent on that of the bath. Reactions between the layer and the solid refractory are slow, as evidenced by the rather good life of the crucible. Hence it seems probable that the layer is more nearly in equilibrium with the metal than with the underlying crucible material and that, once it is established under a bath of a given composition, its further reactions with that bath are slow. Additions to slag or bath may be followed by changes in the layer; and time must be allowed for virtual completion of such changes, before it can be assumed that slag and metal are in equilibrium. We may judge from the results reported that, in general, this was the case and that the data represent at least quite close approximations to slag-metal equilibrium.

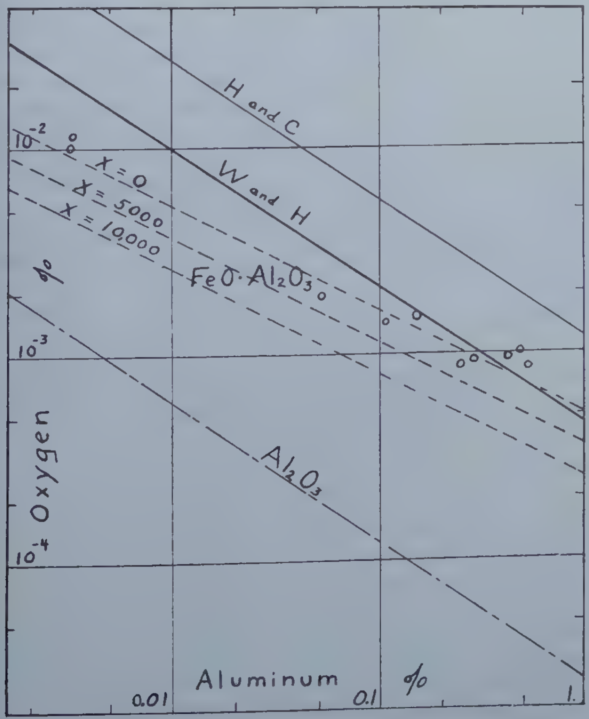

Fig. 21—Aluminum deoxidation diagram showing calculated (lowest) line and experimental (upper) lines.

If the deoxidation product is FeO Al_2O_3 the calculated line is shifted upward to an extent depending upon the (unknown) free energy of formation of the interoxide compound as indicated by the lines X.

Data on deoxidation and on oxygen solubility are no better than the analytical methods employed. The vacuum fusion method as used by the authors seems entirely adequate for the samples analyzed. I have had frequent occasion to compare results with their laboratory, always with very satisfactory agreement. The determination of aluminum at very low concentrations is perhaps an even more difficult procedure. Here also the colorimetric method used has been worked out with great care and is undoubtedly the most dependable method available.

The discrepancy between observed and calculated deoxidation or solubility lines is not to be explained as the result of experimental errors, either in the sampling or analysis of the metal. Nor is it to be blamed upon inaccuracies in the several kinds of indirect data upon which the calculated results were based. It is true that both the observed and the calculated lines admit of some uncertainty as to their exact locations, but the uncertainties are small compared to the wide gap which separates the two lines.

The authors have pointed out the real cause of the discrepancy. In all of their experiments the solid phase was not Al_2O_3 but a mixed oxide containing iron and aluminum. This suggests an extension of the calculated values to include equilibrium with the spinel $FeO \cdot Al_2O_3$. The free energies of FeO and Al_2O_3 are known, that of the spinel is not. However, it cannot differ greatly from that of its component oxides for even in the more stable spinel, chromite, the free energy of formation from the oxides is less than 10,000 cal. For purposes of calculation we shall call this free energy X and solve for values of X lying between zero and 10,000 cal.

The other data required are taken from the forthcoming revision of "Basic Open Hearth Steelmaking" and are given in the following equations in which underlined symbols indicate elements dissolved in liquid steel and the standard concentrations are 1 pct.

		ΔF° at 1600°C, cal
Al_2O_3	$= 2\,\underline{Al} + 3\,\underline{O};$	$+\,107{,}200$
FeO	$= Fe + \underline{O};$	$+\quad 5{,}460$
$FeO + Al_2O_3$	$= Fe + 2\,\underline{Al} + 4\,\underline{O};$	$+\,112{,}660 - X$

The corresponding equilibrium concentrations are shown in fig. 21. The line marked Al_2O_3 corresponds to the first equation, those marked $FeO \cdot Al_2O_3$ correspond to the last, with $X =$ O, 5000 and 10,000 cal, respectively. The two upper lines represent the data of Hilty and Crafts and of Wentrup and Hieber. The points are the observations of Hilty and Crafts in the presence of 0.50 pct Mn.

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The discrepancy between observed and calculated results is thus reduced to the same order of magnitude as the experimental uncertainty, simply by referring both to the same nonmetallic phase. The gap should be further reduced when we have learned the extent to which the activity of oxygen is affected by the presence of aluminum.

At the same time a question is raised which is not easy to answer, namely, why does not Al_2O_3 form as the nonmetallic phase? The calculations and the relative positions of the lines in the figure show that under the experimental conditions Al_2O_3 is a more stable phase than $FeO \cdot Al_2O_3$. What mechanism could have prevented nucleation of the former even when alumina crucibles were used? How can we in practice obtain the theoretically more complete deoxidation corresponding to the formation of Al_2O_3?

J. F. Elliott—The authors are to be commended on their attempt to evaluate the equilibrium of oxygen and aluminum in liquid iron. This is a difficult problem as may be deduced from the few investigations of it that have been reported in the literature.

We, along with many others, have observed that the oxygen content of aluminum-killed steels is far above that computed from existing thermodynamic data on the formation of Al_2O_3. Some explanation of this is necessary.

First I would like to make some observations and then ask some questions on the procedure that will help to augment the necessarily restricted coverage of the experimental work in a paper of this type.

In a system of this sort there is a somewhat greater crucible-metal surface than slag-metal surface, and the probability of obtaining thermal equilibrium at the slag-metal interface is less than at the crucible-metal interface. Consequently it would seem that the layer of reaction product on the crucible is more significant than the slag in this study.

That liquid iron containing 0.002 pct $\underline{Al}$, the end point, can coexist with a phase or phases containing appreciable Fe_3O_4 is an unexpected result. It is interesting to compute the aluminum content of iron in equilibrium with the spinel and alumina from existing thermal data:

$$3.\quad Fe_xO_{(l)} \rightarrow X\,Fe_{(l)} + \tfrac{1}{2}\,O_{2(g)} \qquad \Delta F^\circ = 56{,}830 - 11.9\,T$$

$$4.\quad 2/3\,Al_{(l)} + \tfrac{1}{2}\,O_{2(g)} \rightarrow 1/3\,Al_2O_{3(s)} \qquad \Delta F^\circ = -131{,}100 + 25.3\,T$$

$$5.\quad 2/3\,\underline{Al} \rightarrow 2/3\,Al_{(l)} \qquad \Delta F^\circ = 5{,}100 + 6.7\,T$$

$$6.\quad Fe_xO_{(l)} + 2/3\,\underline{Al} \rightarrow 1/3\,Al_2O_{3(s)} \qquad \Delta F^\circ = -69{,}200 + 20.1\,T$$

$$7.\quad Fe_xO \cdot Al_2O_{3(s)} \rightarrow Fe_xO_{(l)} + Al_2O_{3(s)} \qquad \Delta F^\circ = +10{,}000$$

$$8.\quad Fe_xO \cdot Al_2O_{3(s)} + 2/3\,\underline{Al} \rightarrow 1\,1/3\,Al_2O_{3(s)} \qquad \Delta F^\circ = -59{,}200 + 20.1\,T$$

The thermal data are obtained as follows: Eq 3, Dastur and Chipman;[24] eq 4, chapter 14, Basic Open Hearth Steel Making, 1950 edition; eq 5, Chou and Elliott;[25] eq 7 assuming ΔF° for the spinel formation is the same as for chrome spinel by Chen and Chipman.[26] From eq 8 the iron in equilibrium with the spinel and alumina at 1600°C contains 0.0002 pct Al. A total error of +6000 cal in eq 5 and 7 is required to place the aluminum concentrations at about 0.002 pct. If it were not for the Fe_3O_4 observed in the solid phase, this could be the "end point."

In an isothermal isobaric section of a three-component system the phase rule requires an invariant system at equilibrium with three phases present. It is disturbing that, to the contrary, X-ray study showed Al_2O_3 and $FeO \cdot Al_2O_3$ to be present with iron containing a variable amount of aluminum, that is, 0.10 pct and more.

The slopes of the lines in figs. 8, 11, and 12 may indicate the types of material separating from the melt as the composition is shifted. Fig. 8 indicates a ratio of oxygen to aluminum of 3/2, that of alumina. The slope should be 4/2 for the spinel and a correction for the activity coefficient of oxygen in the presence of aluminum would shift the high aluminum end in the proper direction. For the liquid containing 0.46 pct Mn (fig. 11) the slope is approximately 4/2 and in fig. 12 the ratio is 8/2. Thus again the ratio of [O] to [Al] is surprisingly high.

We would appreciate further comment on the following points.

Would the authors describe the crucible reaction product and its formation in more detail? What was its composition and did it form even when the aluminum concentration in the melt was high, as in runs A-8 and A-12?

From the data sheets for the runs it appears as though the deoxidizer was added to the melt much less often than the oxidizer. We have speculated on why all the runs show a general and pronounced loss of aluminum. Is it connected with the difficulty of obtaining equilibration as described in the section on the crucible reaction? Can the apparent high oxygen pressure in the system be due to the slow evolution of water vapor from the cement and the water of hydration in the soapstone?

In short can it be that the results are discordant because of lack of equilibration? If so, it would seem that the results as they appear in the paper are of doubtful value as equilibrium is essential in a study of this type.

N. A. Gokcen—In view of the experimental technique used in this study it would be of interest to know what method the authors used to establish that there was no oxygen present in their furnace atmosphere. We have found that in argon of commercial grade, oxygen is definitely present, and this can be detected by passing the gas through a deoxidizing or purification train.

Examination of the analytical results of table I shows that at least some of the experimental heats do not represent the equilibrium condition. Towards the end of these runs, a decrease in the aluminum content is not always accompanied by an increase in the oxygen content and vice versa. As two specific examples, we may indicate the runs A-7 and A-9. In these runs the temperature was maintained reasonably constant. The percentage of aluminum and oxygen are within the range of optimum chemical analysis. The variation in deoxidation constants is greater than the probable analytical errors, as shown below:

Run A-7

$(\underline{Al}\%)^2(\underline{O}\%)^3$ products are:

$(0.19)^2(0.0030)^3 = 9.75\text{x}10^{-10}$
$(0.16)^2(0.0072)^3 = 95.5\text{x}10^{-10}$
$(0.12)^2(0.0055)^3 = 24\text{x}10^{-10}$
$(0.087)^2(0.0041)^3 = 5.22\text{x}10^{-10}$

Run A-9

$(\underline{Al}\%)^2(\underline{O}\%)^3$ products are:

$(0.0088)^2(0.027)^3 = 15.2\text{x}10^{-10}$
$(0.0023)^2(0.050)^3 = 6.62\text{x}10^{-10}$

In the case of plain aluminum heats most of the slags were solid. Liquid metal cannot be in equilibrium with respect to slags and alumina crucibles when the activity of Al_2O_3 is not the same in both of these latter phases. Liquid slag can react with liquid iron at a rate very much faster than reaction of alumina crucibles with the metal and can overshadow the effect of crucibles upon equilibrium. (This is not so when slag is solid.) The minimum time for attainment of equilibrium between solid slag (or crust) and liquid metal may well be considerably longer. The authors do not have experimental proof that equilibrium was reached with solid crucible or solid slag, or that the activity of Al_2O_3 was the same in the slag and crucible. This point unfortunately has not been studied in this investigation and leaves some doubt whether or not phases other than pure Al_2O_3 can be in equilibrium with melts containing considerable percentages of aluminum.

Eq 1 does not represent the deoxidation constant of aluminum. This product is at least a function of the activity of Al_2O_3 in the slag phase. The exact equilibrium constant is obviously $K = \dfrac{a^2_{\underline{Al}} \times a^3_{\underline{O}}}{a_{Al_2O_3}}$

C. E. Sims—The attention to details and the technical skill shown in the conduct of these experiments is outstanding and vouches for the accuracy of the results. I wish to offer some corroborative evidence from some experimental work on deoxidation effects, but which was done on a grosser scale.

In a paper entitled "Relative Deoxidizing Powers of Some Deoxidizers for Steel,"[27] evidence was given that, when a certain degree of deoxidation is reached in steel, the sulphide inclusions change sharply from large globules to a fine intergranular eutectic. Deoxidizers were compared by determining the least content that would effect this change. Deoxidation was carried out in 250-lb induction-furnace melts and only 45 sec was allowed after the deoxidizer addition, for reaction and approach to equilibrium, until a sample was taken. Thus, the conditions were quite different than in the experiments just described by Dr. Hilty, but some of the results were similar.

In fig. 6 of the above-mentioned paper,[27] the steels referred to were of the composition: C, 0.25 to 0.30 pct; Si, 0.30 to 0.40 pct; and Mn, 0.40 to 0.60 pct. As will be noted in the figure, the first change from the globular, Type I to the eutectic, Type II sulphides was obtained with a residual Al content of 0.002 pct. Some vestiges of Type I sulphides were found, however, in other samples which analyzed 0.005 pct residual Al. When a medium Mn steel was used, the transition was always sharp and final at a content of 0.002 pct Al. This agrees with the results just given, that with higher Mn, less Al is needed to deoxidize a steel.

When a steel with normal carbon and manganese, but with only 0.04 pct Si, was used, the transition was at the same Al content of 0.002 pct. This indicates that the presence of silicon does not affect the amount of aluminum needed for deoxidation.

With a steel containing normal silicon and manganese, but with a carbon content of 0.07 to 0.09 pct, Type I inclusions were retained consistently up to a residual Al content of about 0.01 pct, or nearly five times as much as for the higher carbon. This indicates that carbon may act much like manganese in aiding the deoxidation with aluminum.

Total oxygen and aluminum determinations made on a medium-carbon steel with a manganese content of 0.58 pct gave virtual checks with the solid-line curve of the authors' fig. 11 in the range of 0.002 to 0.01 pct Al. At higher aluminum contents, the results were above the curve of fig. 11. This close agreement appears to be good evidence that, in a well-circulated steel bath, a homogeneous reaction like dissolved aluminum reacting with dissolved oxygen goes to equilibrium very rapidly. An oxide product of the reaction is precipitated, but the bath is also in equilibrium with the precipitate. There seems little reason to doubt that the authors attained equilibrium in their experiments.

G. R. Fitterer—The authors are to be congratulated for the thoroughness of their work and the excellent manner in which they have written this paper.

In their introductory remarks, they have cited a paper by Herty, Byrns, and myself,[6] but in later paragraphs they state that the only previous experimentally determined "deoxidation constant" for aluminum was reported by Wentrup and Hieber.[8]

As a matter of record, it should be pointed out that an aluminum deoxidation constant was determined and reported by Herty, Byrns, and myself.[6] We expressed this constant in terms of "% FeO in liquid Fe" rather than as dissolved oxygen (O). I have recalculated all of the known constants which have been determined to date on the basis of FeO as shown in table V. The omission of this information from the present paper was probably an oversight on the part of the authors. Also, in all fairness, the data of Hessenbruch is recorded, herewith.

The four experimental constants are essentially checks and the thermodynamic calculation of Herty, Fitterer and Byrns also checks these results quite closely. The thermodynamic calculation of Chipman[11] remains as the only value which does not agree. The difference between these values may be explained by Chipman's assumption regarding the activity of FeO.

The writer is of the opinion, however, that the basic free-energy calculations which Chipman made regarding this reaction are essentially correct. His original free-energy equations[11] were:

$$\Delta F = -382{,}100 + 77.2\,T \text{ for } 2Al_{(l)} + 3/2\,O_2 = Al_2O_3$$

$$\Delta F = -139{,}140 + 19.8\,T \text{ for } 3Fe_{(l)} + 3/2\,O_2 = 3FeO_{(l)}$$

Subtracting:

$$\Delta F = -242{,}960 + 57.4\,T \text{ for } 2Al_{(l)} + 3FeO_{(l)} = Al_2O_{3(s)} + 3Fe_{(l)}$$

Up to this point, the writer thoroughly agrees with Chipman's values. Actually, these do not differ materially from those used by Herty, Byrns and myself.[6]

The equilibrium constant for this reaction should first be expressed as

$$K_T = \frac{(a_{Al_2O_3})\ (a_{Fe})^3}{(a_{Al})^2\ (a_{FeO})^3}$$

in terms of activities of the various constituents, then in accordance with standard thermodynamic procedure

$$\Delta F = -242{,}960 + 57.4\,T = -4.575\,T \log K_T$$

and at 1600°C ($T = 1873°K$), $K_T = 6.31 \times 10^{15}$.

Unless it can be proved that the formation of the spinel (FeO Al_2O_3) appreciably affects the activity of Al_2O_3 as Hilty and Crafts suggest, then the activities of Al_2O_3 and Fe may be assumed to be unity. Incidentally, the formation of such compounds was also noted in our paper.[6]

Chipman found that the activity coefficient of aluminum in liquid iron was 0.68, by means of an ingenious experiment in which the distribution ratio of aluminum between two immiscible liquids (i.e., iron and silver) was determined. Hence, $a_{(Al)} = 0.68\,N_{Al}$ wherein N_{Al} is the mol fraction of aluminum in liquid iron.

Now if one may assume for the moment that $a_{FeO} = N_{(FeO \text{ in liquid iron})}$, the equilibrium constant may be expressed as

$$K_T = \frac{1}{(0.68\,N_{Al})^2\ (N_{FeO})^3} = \frac{1}{\left(\dfrac{0.68\%\ Al}{27 \times 1.79}\right)^2 \left(\dfrac{\%\ FeO}{71.8 \times 1.79}\right)^3}$$

wherein 27 and 71.8 are the atomic and molecular weights of aluminum and FeO, respectively, and 1.79 represents the total mols (i.e., 100 pct Fe/55.84).

Hence

$$K_D = (\%\ Al)^2\ (\%\ FeO)^3 = \frac{1}{K_T\ (2 \times 10^{-4})\ (4.7 \times 10^{-7})}$$

and since $K_T = 6.31 \times 10^{15}$ then $K_D = 1.67 \times 10^{-6}$. This constant is identical with our thermodynamic calculation (No. 3, table V) and is much more in agreement with the experimental values and is to be compared with Chipman's[11] calculated constant (i.e., 2.2×10^{-13}). Chipman has modified this value slightly from time to

Table V. Deoxidation Constants for Aluminum Arranged in Chronological Order

No.	Authors	$K_D = (\% \text{ Al})^2 (\% \text{ FeO})^3$	Source
1	Hessenbruch	5.6×10^{-6} (Avg.)	Experimental *Revue de Met.* (Mem.) (1929) 26, 93.
2	Herty, Fitterer and Byrns[6]	5.7×10^{-7}	Experimental
3	Herty, Fitterer and Byrns[6]	0.17×10^{-7}	Thermodynamic calculation
4	Chipman[11]	2.2×10^{-13}	Thermodynamic calculation
5	Wentrup and Hieber	1.0×10^{-8}	Experimental
6	Hilty and Crafts	2.7×10^{-7}	Present paper
7	Average of all experimental constants	2.26×10^{-7}	

time,[23] but in general the difference between his and the experimental values is of about the same order of magnitude.

The reason for the difference between Chipman's[11] original calculation and those given herein is merely in the expression of the activity of FeO or in other words the expression of the free energy of solution of FeO in liquid iron. In the above calculation, it was suggested and assumed that $a_{(FeO)} = kN_{FeO}$ in accordance with Henry's law. Further, it was assumed that k or the activity coefficient is very nearly equal to unity. Hence, the solution of FeO (or oxygen) in the extremely small quantities at equilibrium with aluminum in liquid iron is nearly perfect or extremely dilute.

The concept which Chipman apparently used is that the activity of FeO in liquid iron is affected by its saturation limit. Hence

$$a_{FeO} = \frac{N^e_{FeO}}{N^o_{FeO}}$$

wherein N^e_{FeO} is its mol fraction in the standard state or the saturated solution. This was essentially equivalent to

$$a_{FeO} = \frac{(\% \text{ FeO})_e}{(\% \text{ FeO})_{sat.}}$$

and since the percent FeO in the saturated or standard state was about equal to unity, then Chipman assumed that

$$a_{FeO} = \% \text{ FeO}$$

This was a logical assumption on Chipman's part at the time. However, in view of the agreement between the experimental constants, this concept of the activity of FeO should be reconsidered.

In addition to the above, the writer is of the opinion that the mechanism of the aluminum deoxidation process is somewhat different from that encountered in other deoxidizers, i.e., the velocity of oxidation of aluminum is greater than its rate of diffusion. Hence, when aluminum is added to steel, the resultant deoxidation is not uniform as it is in the case of silicon, for example. Instead, the steel in the immediate area of an aluminum particle is highly deoxidized in accordance with a reaction with essentially 100 pct aluminum. The remaining deoxidation is dependent upon diffusion of aluminum throughout the steel (or of the oxygen to the concentrated area containing the aluminum). However, either or both of these diffusion processes may be retarded by the presence of the Al_2O_3 which reduces the metal fluidity.

Localized deoxidation has been observed by any one who has added aluminum pellets to large ingots. This effect may cause the experimental constants given in the table to be "average" or "apparent" constants which, however, approximate the practical conditions and are thus industrially important. Classical thermodynamic treatment of reactions is most useful and generally accurate unless some factor such as a low diffusion rate prevents normal equilibrium to be established within reasonable periods of time.

D. C. Hilty and W. Crafts (authors' reply)—It is the authors' conviction that much of the discrepancy between thermodynamic prediction and actual observation of steel deoxidation may be due to incomplete understanding of the basic assumptions regarding the reactions of the participating phases. As knowledge of the nonmetallic phases that can coexist with steel increases, this disagreement may be expected to diminish. We are gratified that Dr. Chipman shares this opinion. His discussion appears to help rationalize the theoretical approach with our empirical treatment of oxygen solubility.

In reply to requests to give more specific details regarding composition of the crucible reaction product, the product formed even when the aluminum concentration in the melt was high, as in runs A-8 and A-12, but, unfortunately, samples of it always contained so much metal that chemical analyses were meaningless. Actually, samples of the reaction product taken at operating temperatures appeared to reject metal on cooling.

Mr. Elliott is correct in presuming that in many of the runs the oxidizer was added more frequently than the deoxidizer. This was done as a matter of convenience to assist in obtaining clean samples, but it had no observed influence on the final results. We found that when large aluminum additions were made to an oxidized bath, the immediate local reaction occurring at the surface of the heat before equilibrium was attained produced a heavy crust of reaction product over the bath that made sampling difficult. Such a condition did not occur to as serious a degree when ferric oxide was added to a bath containing aluminum.

With respect to the question of Messrs. Elliott and Gokcen in regard to substantial attainment of equilibrium, runs A-12 and A-14 in table I are illustrative. The last four samples of run A-12 and the last three samples of run A-14 cover periods of approximately 3 hr and 1½ hr, respectively, during which time no additions were made to the heats, and there were no significant changes in composition. It is felt that divergence from the anticipated reaction is of greater significance in the experimental results.

Mr. Sims has presented interesting observations tending to corroborate our results. We can only speculate regarding the significance of Type II sulphide inclusions as related to oxygen solubility, but we are pleased to learn that Mr. Sims' analytical results agree well with ours.

The interpretation by Dr. Fitterer of the thermodynamics of aluminum deoxidation is interesting, but it is considered that, like the postulations of the other discussers, it will be necessary to supply more tangible evidence to support an acceptable rationalization of the reaction. Although the results of Herty, Fitterer and Byrns, and Hessenbruch were corroboratory, they were not cited because the conditions under which the data were obtained were not controlled with the laboratory degree of accuracy of temperature and composition that is required to support empirical data that differ so widely from theoretical expectation.

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Solubility of Oxygen in Liquid Iron Containing Silicon and Manganese

by D. C. Hilty and W. Crafts

DISCUSSION, K. L. Fetters presiding

L. S. Darken—Laboratory investigation of deoxidizing and other steelmaking reactions is usually centered, at least first, on the determination of the equilibrium or equilibria involved. This seems a reasonable procedure since equilibrium, if attained, depends only on composition, temperature, and pressure; hence conclusions derived from data on small experimental quantities are applicable to a heat of steel providing equilibrium is attained in both cases. A knowledge of equilibrium serves as a useful framework even though we may know that practical conditions do not correspond to complete equilibrium. On the other hand, nonequilibrium or rate phenomena depend on a wider variety of conditions and are more difficult to interpret; conclusions applicable to laboratory conditions may or may not apply to larger scale phenomena. Hence the attainment or nonattainment of true equilibrium in the experiments here reported is of critical importance in evaluating their significance. Since some of the statements in this paper and in the closely related preceding one (on aluminum deoxidation) imply some doubt on this matter, I should first like to ask the authors whether their conditions are intended and believed to represent equilibrium.

I should like to point out three considerations which seem to cast considerable doubt on the achievement of equilibrium, at least of the particular equilibrium under consideration.

1. In the experiments on manganese deoxidation the authors point out that they could not maintain the manganese-oxide slag on top of the metal in their rotating crucible, and hence they substantially dispensed with this slag. This leads to serious trouble in the interpretation of the results, for any equilibrium is, of course, a particular specific equilibrium—in this case

$$\underline{Mn} + \underline{O} = MnO$$

The experimental deletion of the upper layer of manganese oxide means that if equilibrium is attained at all it is attained between the metal and the MnO which has soaked into or adhered to the crucible (under the metal) and has dissolved substantial amounts of the crucible material including impurities. These impurities may constitute a significant portion of the slag by virtue of the small total amount of slag, even though the crucible is relatively pure. Hence there would seem to be a strong presumption that the equilibrium (if attained) involves not a pure MnO (or MnO — FeO) slag but one saturated with alumina and containing perhaps considerable impurities which substantially lower the concentration and activity of MnO, causing the above reaction to proceed to the right further than it would in the absence of alumina and impurities. Hence it is not surprising that manganese here appears as a better deoxidizer than found by other investigators. The present results may represent equilibrium with a slag of unknown composition which seems unlikely to be particularly related to plant experience.

2. The curves representing the observed silicon deoxidation (figs. 3, 4, and 5) are all drawn with a discontinuity in slope at about 0.02 pct oxygen. This point is interpreted as corresponding to the three-phase equilibrium, metal, slag, solid silica. The type of construction shown in these figures (though apparently fitting the data) is contrary to a fundamental principle of heterogeneous equilibrium as pertains to the construction of phase diagrams. According to this principle, the two solubility curves (each of the two portions of the curves in figs. 3, 4, and 5) must intersect in such manner that their (metastable) extensions must lie outside the homogeneous field rather than inside as in these figures. In other words, the "point" in these curves should be aimed in the opposite direction, if it is to be interpreted as corresponding to the three-phase equilibrium. The construction adopted is in violation of the second law of thermodynamics. This matter is discussed in detail in several texts and also by Lipson and Wilson.[19] The same criticism applies to the later figures representing conditions for manganese additions.

The occurrence of this discontinuity or break at 0.02 pct oxygen casts further doubt on its interpretation. The earlier investigation of this system by Körber and Oelsen is in substantial agreement with the several recent findings of Chipman and coworkers that the oxygen content of iron in equilibrium with silica and silica-saturated iron oxide slag is about one third to one half that (0.24 pct at 1600°) of iron saturated with pure iron oxide; thus there seems reliable evidence that iron saturated with silica and iron silicate slag at 1600° contains about 0.1 pct oxygen, or certainly much more than the 0.02 pct proposed in this paper.

3. In the quarternary system iron-silicon-manganese-oxygen one of the equilibria involved may be written

$$2\,\underline{Mn} + SiO_{2\,(solid)} = 2\,MnO_{\,(slag)} + \underline{Si}$$

The activity of SiO_2 is constant (if equilibrium is attained) by virtue of its presence as a substantially pure solid. At not too low metallic manganese content, the activity of MnO in the slag is constant by virtue of the fact that the slag is substantially pure manganese silicate saturated with silica and hence of constant composition. Thus the equilibrium constant for the above reaction is a_{Si}/a^2_{Mn}. Barring unanticipated large changes in the activity coefficients, the equilibrium constant may be adequately approximated for the composition range covered as [% Si]/[% Mn]^2. Thus a plot of log [% Mn] against log [% Si] would be expected to be linear with a slope of one half as found by Körber and Oelsen. In the present investigation the slope (shown in fig. 15) is found to be one. It is difficult to believe that this finding represents a correct equilibrium determination, since it is at odds both with prior experimental investigation and with theory.

In view of the above points it seems that, although this paper reports many interesting findings, there is room for considerable skepticism as to the attainment of equilibrium and as to the conclusions drawn.

N. A. Gokcen—The authors consider that $\underline{Si}\% \times \underline{O}^2\%$ product is constant. This product is a function of the activity of SiO_2. The true constant is $\dfrac{a_{\underline{Si}} \times a_{\underline{O}}}{a_{SiO_2}}$. If the slags of this investigation were always saturated with SiO_2 then $\underline{Si}\% \times \underline{O}^2\%$ product would be constant,

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[19] Lipson and Wilson: *Journal* Iron and Steel Institute. (1940) 142, 107.

since the activity of SiO_2 of such slags is the same as the activity of pure SiO_2. There is no experimental evidence indicating that these slags were saturated with SiO_2. The only method of insuring such saturation is to keep solid silica in contact with these slags.

In referring to figs. 3, 4, and 5 of this paper it is difficult to justify a break in the logarithmic plots of oxygen vs. silicon through such scattered points. A straight line can be drawn quite satisfactorily without a break at any concentration of silicon. Furthermore, the interpretation of this breaking point as the invariant point is against the well-known phase rule: $F = C - P + 1$, $C = 3$ (oxygen, silicon, iron), $P = 3$ and $F = +3-3+1 = 1$. Therefore, when the temperature is held constant, F is zero in agreement with the definition of the invariant point. Now if the silicon concentration is varied beyond 0.05 pct Si at 1600° as shown in fig. 4, one of the phases must disappear. This apparently was not observed by the authors. Perhaps the end point as referred to in this paper (p. 429) is closer to the invariant point. An entirely different technique shows that Körber and Oelsen's invariant point is fairly accurate, and there is no discontinuity in the silicon deoxidation curve at and below 0.05 pct silicon.

G. Derge—In view of the previous discussion, it should be pointed out that the data presented in these papers were obtained under careful laboratory control of many factors such as materials and temperature and that they appear to be reproducible within narrow limits. They should therefore be accepted as experimental facts. The experiments represent the actual circumstances encountered in steelmaking much more closely than the hypothetical situations required by the assumptions involved in any thermodynamic calculation of similar data. It therefore behooves us to recognize that differences between the experiment and the calculation can be attributed to an incomplete accounting of the factors involved in the experiment. The experimental data cannot be regarded as faulty just because they represent a real rather than a hypothetical situation. These statements are not intended to depreciate either the experimental or theoretical approach of this problem, but only to emphasize that each has its value and that our knowledge is incomplete until both can be used to attain the same end result.

D. C. Hilty and W. Crafts (authors' reply)—The authors are in complete agreement with Dr. Darken's first point regarding the effect of alumina (from the crucible) on equilibrium in the Fe-Mn-O system. In fact, during preliminary work on this system a few observations of such an effect were made. It was for this reason that, as stated in the paper, the study of the limiting effect of manganese on the solubility of oxygen in iron was done entirely in magnesia crucibles. It is believed that at the temperatures involved, the solubility of MgO in the MnO-FeO slag is so low that it has only a small effect on the activity of MnO. In regard to his second point, it was recognized that the breaks in the logarithmic silicon curves apparently point in the wrong direction according to current concepts of thermodynamic activities. Nevertheless, since there was rather positive evidence of a phase change at those breaks, and since the full significance of the breaks is not understood, we constructed the curves according to the data. Lipson and Wilson showed that in an isothermal, isobaric section of a ternary system the prolongations of intersecting field boundaries must either both fall within the three-phase region or both fall without the three-phase region and include an angle (on the triangular plot) of less than 180° on the side next to the three-phase region. Within the limits of the experimental uncertainties, the curves fulfill these requirements. We were unable to find evidence that the metal phase was saturated with silica at silicon contents below these breaks, although a steady state of apparent equilibrium was attained, as described in the paper, which agreed well with similar observations by Körber and Oelsen and by Chipman and coworkers. His third point, while based on classical thermodynamics, appears to presume a hypothetical situation. In no instance did we observe even a relatively pure manganese silicate slag such as would be necessary for the reaction he postulates. Moreover, Körber and Oelsen likewise assumed that the equilibrium constant should be

$$\frac{(\%\ MnO)^2 \times (\%\ Si)}{(\%\ Mn)^2}$$

and drew their curve accordingly, although their data could have been fitted equally well by curves of other slopes.

We appreciate Mr. Gokcen's criticisms, but feel that the points he has raised are adequately covered in the paper.

Dr. Derge's comments emphasize the empirical nature of our approach to this problem. While current thermodynamic concepts were recognized in the experimental work and in the interpretation of the results, no compromise was made with the data to conform to preconceived assumptions. It is recognized that the specific experimental method used to attack the problem may have distorted the basic reactions, but the nature of such possible errors in the design of the experimental method has not been suggested. Within the limitations of the method, the data are believed to represent the empirical solubilities of oxygen in the presence of silicon, manganese, and aluminum with a useful degree of accuracy.

Thermodynamic Properties of Sulphur in Molten Iron-Sulphur Alloys

by C. W. Sherman, H. I. Elvander, and J. Chipman

DISCUSSION, D. J. Girardi presiding

J. F. Elliott—This is an excellent piece of work and makes a chemical metallurgist more enthusiastic than ever about what can be done with multicomponent systems, if we have satisfactory data.

I have a remark to make on the interpretation of fig. 5. First, I will comment on the problem of activities in solutions. The iron-sulphur system has in its phase diagram an intermediate solid phase FeS. The occurrence of an intermediate phase is normally associated with negative departures from Raoult's law over a portion of the activity curves in the liquid. (Perhaps it would be better to reserve the phrase "departure from ideality" to departures from Raoult's law line rather than to departures from Henry's law line).

Fig. 5 indicates that the deviation of the sulphur activity curve from the Henry's law line is negative;

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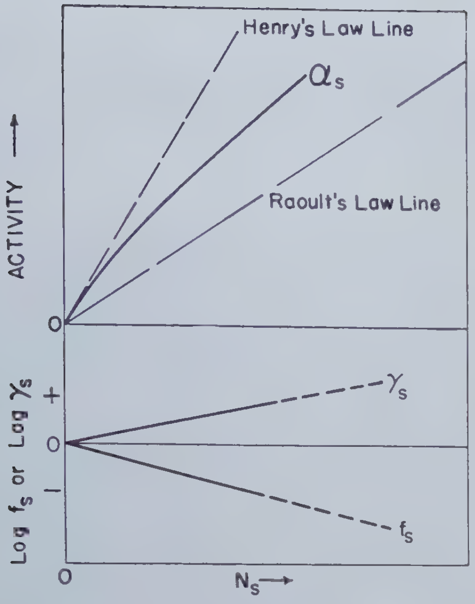

Fig. 9—Dependence of activity coefficients on the choice of standard state.

that is, that f_s is less than one; the standard state being the infinitely dilute solution. Fig. 9 shows that this may actually be a positive deviation from ideality (the Raoult's law line) of the activity curve based on pure sulphur as the standard state. The activity coefficient, γ_s, may then be greater than one.

On this basis the activity curve for sulphur (based on pure sulphur as the standard state) may have a positive deviation from ideality at low concentrations and then crosses the ideal line and becomes negative at higher concentrations. Successively lower values of log f_s in fig. 5 may mean that the radius of curvature of the activity curve becomes smaller as the temperature rises even though the Henry's law line approaches the Raoult's law line. The activity curve should approach the Raoult's law line with increased temperature, but it is somewhat complex in this case; and if we look only at a small portion of the curve as represented by fig. 5, the general trend may be obscured. Consequently the decrease in log f_s with increased temperature may not be contrary to theoretical expectations.

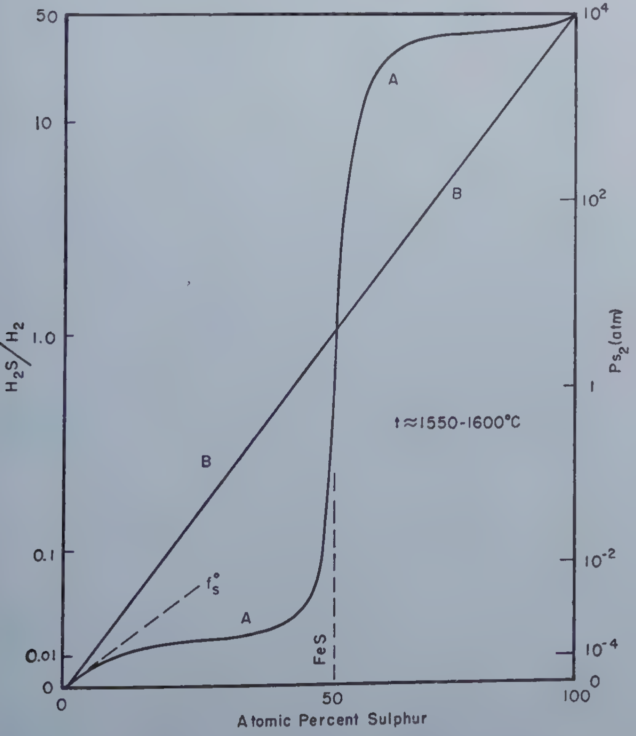

Fig. 10—Escaping tendency of sulphur in the system iron-sulphur, curve *A*.

Curve *B* corresponds to an ideal solution. For clarity the ordinate scale is nonlinear, and the H_2S/H_2 ratios and the sulphur pressures are approximate values.

J. E. Stukel—I would like to ask the authors just one question. They are very concerned about the effect of silicon and other elements in the molten iron on the activity of the sulphur. Do the authors have any information on the effect of the dissolved hydrogen on the activity of sulphur in molten iron?

T. Rosenqvist—I would like to make a comment because I have myself been working a little with the extended part of the system iron-sulphur. The escaping tendency of sulphur runs like curve *A* on fig. 10. (The fact that the reference state "pure sulphur" is undefined at temperatures above the critical temperature of liquid sulphur, is without importance in this connection.) In the middle of the system, the sulphur pressure increases by several orders of magnitude as one goes through the stoichiometric composition FeS.

For an *ideal* solution of sulphur in iron one should expect the sulphur pressure to run as indicated by the diagonal, *B*, (fig. 10). This curve has a considerably higher slope than the one experimentally found for a diluted solution of sulphur in liquid iron, f_s°.

If one assumes that the system iron-sulphur becomes increasingly ideal with increasing temperature, one should expect an increasing slope and a straightening out of the experimental curve. This would be in disagreement with fig. 5 of the paper.

I would like to add that an increasing deviation from ideality with increasing temperature is *not* in violation with any fundamental thermodynamic law. It would correspond to the appearance of liquid immiscibility between iron and FeS at higher temperatures. Immiscibility regions with a lower critical point are known, but they are rather rare and in the present case such a behavior must be regarded as rather improbable.

C. W. Sherman (authors' reply)—The authors are indebted to all the discussers. There are several comments that I would like to make. We were worried about the interpretation of this deviation from ideality, and, as we say in the paper, it was tentative. We would still like to think about it some more.

As to Dr. Stukel's comment about hydrogen, one investigation always influences another. I happened to be doing this work at the same time Dr. Carney was investigating hydrogen solubility. As you remember, he found that it was very difficult to sample at partial pressures of hydrogen of, say, a quarter of an atmosphere for the simple reason that as the metals solidify in the sample wall, the hydrogen coming out of solution literally squirted the metal out of the sampler, so that all he had left was a thin tube like a tin can. The same thing happened to me. When the sulphur content of the melts went below 0.3 pct, the hydrogen solubility increased and I could not get a good sample at less than 0.25 pct sulphur. We felt that this was sufficiently low. However, if it were desired to go to lower percentages, the argon content of the gas could be increased to a point where the hydrogen content was rather low and one could get into a sufficiently good sampling range. As you decrease the partial pressure of the hydrogen, you increase the dissociation of H_2S, so that you have to take a combination of favorable factors. Since the results indicated that there is a straight-line relation at low percentages of sulphur, we did not go any lower.

As to the actual concentration of hydrogen in our sulphur samples, we do not know that. As to the oxygen concentration, we do not know that. We have made every attempt to keep oxygen out. These equilibria will probably be the subject of further research.

The Effect of Carbon on the Activity of Sulphur in Liquid Iron

by J. P. Morris and R. C. Buehl

DISCUSSION, D. J. Girardi presiding

F. D. Richardson—The authors are to be congratulated on this further contribution to our knowledge of the thermodynamics of the interaction between sulphur and carbon and silicon in liquid iron.

As the authors state, the influence of carbon and silicon on the activity coefficient of sulphur in liquid iron is clearly of great importance in the blast furnace, since it must cause a three to fourfold improvement in the partition of sulphur between slag and metal. The influence of increasing temperature in further increasing the activity coefficient of the sulphur in the metal in the blast furnace by increasing the carbon content is also of interest. This effect, however, is probably only part of the reason for the general observation in blast furnace practice, that the sulphur content of the metal is lowered by increasing temperature. Other contributing factors are the lowering of the oxygen potential in the presence of carbon by increasing temperature and the probable increase in the activity coefficient of the lime in the slag for the same reason. The former of these effects, which works via the (CaO) + [S] = (CaS) + [O] equilibrium, might possibly account for a 70 pct improvement in the sulphur partition[9] and the latter might give a further 50 pct improvement.

C. Sherman—I would like to compliment the authors on their very careful research. If I may, I would like to show results of calculations on the carbon-sulphur-iron system similar to the ones that were shown in our paper for the silicon-sulphur-iron system.

For Fe-S-C ternary system

$$K = \frac{P_{H_2S}}{P_{H_2}} \times \frac{1}{(f_s{}^{\circ})\ (f_s{}')\ (\%S)}$$

where f_s = sulphur activity coefficient

$f_s{}' = f_s$ for Fe-S system of equal pct S

$f_s{}^{\circ} = \dfrac{f_s}{f_s{}'}$ for Fe-S-C ternary system

This same analysis has been used on other systems, but the results shown in fig. 7 are for carbon and silicon.

L. S. Darken—I would like to make two brief comments in addition to complimenting the authors on an apparently very precise and accurate investigation.

The first is that the present work is in agreement with a calculation by Larsen and myself.[10] Our calculation (much less precise than the present work) was based on: (1) Unpublished work on the sulphur content of molten iron (1.5 pct at 1500°C) in equilibrium with graphite and an iron sulphide slag; (2) the distribution coefficient of sulphur between slag and carbon-free liquid iron. We expressed the result in a form equivalent to

$$\log \gamma_s = 0.18\ [\%C]$$

which gives an activity coefficient (γ_s) of sulphur only slightly higher than the authors find and certainly within the precision of the earlier work.

My second comment concerns the correlation of the thermodynamic findings with atomistics. A rough picture of the atomic arrangement in the liquid solution is rather easily conceived for this particular liquid solution containing iron, carbon, and sulphur. Carbon has a very much stronger affinity for iron than for sulphur. Hence we may conclude that a sulphur atom will but seldom be adjacent to a carbon atom—since this would be a position of high energy. From the metallic radii of iron and carbon we know that six iron atoms pack neatly around one carbon atom. Thus each carbon atom in retaining this shell of iron atoms (which latter may not be replaced by sulphur on account of the high energy requirement) decreases the available positions for each sulphur atom by six. Hence each atomic percent of carbon decreases the equilibrium sulphur content by 6 pct (of itself). Or, at low concentration each atomic percent of carbon increases the activity coefficient of sulphur by 6 pct. This is in good agreement with the observed increase (6 or 7 pct at low carbon content). It is indeed gratifying to find a case where, by such simple reasoning, quantitative agreement is found between precise data and the modern picture of the atomistics of the metallic state.

F. D. RICHARDSON, British Iron and Steel Research Association, London, England; C. SHERMAN, Massachusetts Institute of Technology, Cambridge, Mass.; L. S. DARKEN, U. S. Steel Corp. Research Lab., Kearny, N. J.

J. P. Morris (authors' reply)—We would like to point out that there is an error in the equation on p. 322 of the paper. The third equation should read:

$$\tfrac{1}{2}S_2\ (\text{gas}) + H_2\ (\text{gas}) = H_2S\ (\text{gas})$$

The authors wish to thank everyone for the interest they have shown in the paper. In regard to the general observation in blast furnace practice, that the sulphur content of the metal is lowered by increasing the temperature, Dr. Richardson is correct in stating that the cause can be attributed only in part to the increase in activity coefficient of sulphur resulting from the rise in carbon plus silicon content of the metal with rise in temperature. However, this factor is probably an important one. The results of one experiment, performed since this report was written, indicate that at a constant temperature the addition of silicon to a melt saturated with carbon causes an increase in the activity coefficient of sulphur even though the carbon solubility is lowered. In this test, 2.5 pct silicon was added to a melt saturated with carbon and maintained at 1400°C. Although the carbon content dropped from 4.85 to 4.1 pct, the activity coefficient of sulphur was increased by about 20 pct.

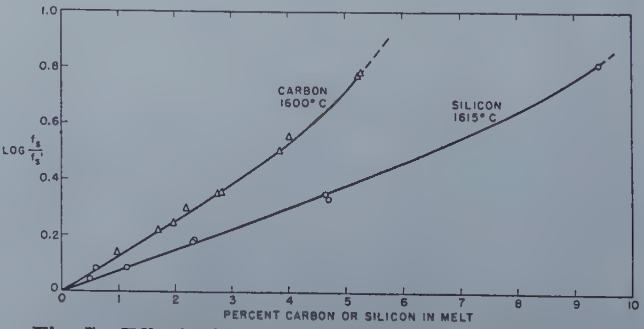

Fig. 7—Effect of carbon and silicon on the activity coefficient of sulphur in iron.

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[9] F. D. Richardson and J. H. E. Jeffes: *Journal* Iron and Steel Institute. (1949) 163, 412.

[10] B. M. Larsen and L. S. Darken: *Trans.* AIME (1942) 150, 87-109.

Side-blow Converter Process for the Production of Low Nitrogen Steel Ingots

by R. R. Webster and H. T. Clark

DISCUSSION, M. W. Lightner presiding

A. B. Wilder—I want to ask one question. On this matter of carbon content, the final carbon content on surface blowing ran higher than in conventional bottom blowing. It was not clear to me just what the factors were that controlled the final carbon content. The reason I ask this question is in making butt-welded pipe, we feel the carbon content should be at a low level to prevent laminations, which are related to carbon segregation. I think the level of carbon would be a factor in the manufacture of the butt-welded pipe, if the process described were to replace the conventional bottom-blown Bessemer vessel.

R. R. Webster (authors' reply)—The carbon value does not result either from a short after-blow or by turning down the converter before the reaction is finished. We have tried to reduce the carbon by extended surface blowing in some cases, but the higher carbon seems to be characteristic of the process as far as we carried it. The carbon can be reduced, of course, at the end of the blow by tipping the tuyeres underneath the surface of the bath and blowing for a few seconds, and that would be the procedure we would recommend at present for getting the carbon as low as possible.

M. W. Lightner—Do you notice any difference in the nitrogen content between heats which are blown by subsurface blowing during the entire course of the heat or those which are surface blown during the early stages and then are subsurface blown during the latter stages of the heat?

R. R. Webster—I showed a couple of distribution curves giving subsurface vs. surface blowing, and in those cases there was a definite difference in the average nitrogen content. The use of subsurface operation at the very end of the blow, i.e., combination blowing, does show a slight pickup in nitrogen. Of the 185 blows made, only 19 were produced with various amounts of subsurface and surface operation, and we did not explore this point as fully as we might have done.

R. A. Flinn—Why was the temperature higher with side blowing than with bottom blowing?

R. R. Webster—We think it is because in the carbon blow of a normal bottom blow converter, the carbon is burned to carbon monoxide; the carbon monoxide is then burned to carbon dioxide outside of the vessel. In surface operation, much of the carbon monoxide is burned to carbon dioxide inside the vessel, and additional heat is obtained thereby.

A. B. WILDER, National Tube Co., Pittsburgh, Pa.; M. W. LIGHTNER, Carnegie-Illinois Steel Corp., Pittsburgh, Pa.; R. A. FLINN, American Brake Shoe Co., Mahwah, N. J.

Experimental Operation of a Basic-lined Surface-blown Hearth for Steel Production

by C. E. Sims and F. L. Toy

DISCUSSION, D. R. Loughrey presiding

I. A. Sirel—I would like to ask Mr. Sims what would the preferred hot metal analysis be as far as manganese and silicon are concerned if you used specially made iron for this process instead of basic iron.

C. E. Sims (authors' reply)—A preferred composition would contain somewhat less silicon than the basic pig iron used in these experiments. High silicon requires a large lime addition. Lime must be added in sufficient quantity to neutralize the silica formed and to leave an excess for dephosphorization.

Manganese presents almost no problem in operation. It is almost completely oxidized and, in burning, develops considerable heat. The evidence indicates, however, that, in continuous commercial operation, there will be an excess of heat produced, and the bath will need to be cooled in some manner as by the addition of scrap or by utilizing the energy for the direct reduction of ore.

There do not seem to be any serious limitations on composition of pig iron. One heat was made with an iron containing 2.27 pct silicon and the phosphorus finished at 0.007 pct. In another, the iron contained 0.45 pct phosphorus which was lowered to 0.019 pct. This indicates considerable leeway in composition.

D. R. Loughrey—We are all very much interested in the recent discovery of very large deposits of iron ore both in Labrador and in Venezuela. I would like to ask Mr. Sims if the iron ore at either or both of these places is such that it would lend itself to the manufacture of iron suitable for use in the turbohearth.

C. E. Sims—According to my information, those ores are not essentially different from ores now used in this country for making basic pig. They should, therefore, be adaptable to this process.

D. I. Brown—You have spoken about the leeway, or spread in analysis of the various irons you can use in the vessel. I would like to have you tell us, if you can, about the different kinds of steels which can be made in such a vessel. The turbohearth process, or it might more aptly be called pneumatic openhearth, is a little different from that used in most Bessemer shops and in the one in which I worked. If we had a blow in the air over 10 min, the boss was in the pulpit in a hurry

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I. A. SIREL, Youngstown Sheet and Tube Co., East Chicago, Ind.; D. R. LOUGHREY, Jones and Laughlin Steel Corp., Pittsburgh, Pa.; D. I. BROWN, The Iron Age, New York, N. Y.; F. C. SENIOR, The Koppers Co., Chicago, Ill.; F. LATHE, National Research Council, Ottawa, Ont.; F. E. VAN VORIS, Bethlehem Steel Co., Bethlehem, Pa.; M. TENENBAUM, Inland Steel Co., East Chicago, Ind.; G. R. FITTERER, University of Pittsburgh, Pittsburgh, Pa.; R. A. FLINN, American Brake Shoe Co., Mahwah, N. J.; S. J. CRESSWELL, Carnegie-Illinois Steel Corp., Chicago, Ill.; J. L. MYER, Temple University, Philadelphia, Pa.

wanting to know what we were doing with the vessel in the air all that time. Mr. Clark showed, on a 22,000 lb heat, a heat time of about 30 min, so if and when the turbohearth gets in commercial production, I suppose we can expect longer heat times. This implies that instead of all low-carbon bessemer steels, and they have been pretty dominantly that, they might be augmented with steels of higher carbon. If you want to get higher carbon you have to recarb, and there are limits, but with bigger heats and longer time, will the turbohearth be able to catch heats on the way down? I do not mean on the button, but if you wanted a 30 carbon heat, and looking at the controls now possible, will such controls be good enough to permit turndown at 25 carbon, recarb to 30 and thus catch heats on the way down?

C. E. Sims—The basic process is best adapted to the production of low-carbon steels for the reason that the natural end point, where the abrupt flame drop takes place, occurs at a carbon content of 0.04 to 0.05 pct. The flame drop is the first and only sign of any definite carbon content.

After the silicon was oxidized, the normal rate of carbon drop was about 0.5 pct per min, and this rate was maintained right up to the flame drop. This is approximately a point a second, and it shows the extreme difficulty of estimating and then stopping on a definite carbon content. Even though the blast were to be suddenly stopped at, say, 0.5 pct carbon, the boil would not stop but would continue at a slowly decreasing rate. It should also be pointed out here that dephosphorization continued up to the flame drop, and heats stopped sooner would have higher phosphorus contents. With present knowledge, it appears quite impracticable to catch carbon on the way down.

As to the time element, it was shown rather clearly in the experimental work that the total air per unit weight of iron was a constant and that the time required for blowing is, therefore, an inverse function of the rate of air input. When the blast rate was increased or the air was enriched with oxygen, the time for blowing was decreased proportionally. The optimum time for blowing a commercial size turbohearth heat is still unknown, but there is reason to assume that it need not be over 15 to 20 min.

F. C. Senior—I would like to ask Mr. Sims his opinion of the effect of normal Thomas phosphorus content (1.8 to 2.2 pct) on the side-blown basic process. All the tests cited were in the order of 0.25 to 0.45 maximum.

C. E. Sims—In my opinion, there would be no unique problem in attempting to process pig iron of normal Thomas phosphorus content by the turbohearth method. Without much change in practice, it is probable that about the same proportion of phosphorus would be removed, resulting in a finished metal containing 0.05 to 0.06 pct. It is my understanding that the Thomas process has difficulty in obtaining phosphorus contents below about 0.05 pct. On the other hand, a two-slag process, such as was described in the paper, might have a definite advantage in handling such high-phosphorus content and lowering it to a desirable end value.

F. Lathe—There are two questions I would like to ask. One of the advantages of using this type of converter appears to be that you can develop more heat in it. If you burn only to carbon monoxide, you develop about 28 pct of the heat, and I judge from the analyses that Mr. Sims has given, that he has developed 55 to 60 pct of the total potential heat of the carbon. Is there any reason why you could not introduce air above the level of the metal and burn all to carbon dioxide and thereby develop substantially 100 pct of the heat of the carbon?

The second question has to do with the use of iron ore or scrap. Obviously, if we develop more heat, we can melt more scrap. Mr. Sims has referred, however, to the use of iron ore, and that is what I am particularly interested in at the moment. I wonder if he would be in a position to say anything further on that subject?

C. E. Sims—Presumably, air could be introduced higher up to complete the combustion. In his patent, on a vessel for surface blowing, Tropenas showed a second row of tuyeres above the first. I have no record of the results obtained with such a device, but it apparently was used very little if at all. Perhaps if the heat is generated too late, it just heats the stack. We believe the turbohearth develops more nearly 80 pct of the potential heat of the carbon.

As mentioned earlier, it appears likely that there will be excess heat developed in commercial operation. This could be utilized in melting scrap or reducing iron oxide. The reduction of iron oxide with carbon is slightly endothermic and could use some of the heat. The experiments were not extensive enough to show how much ore could be used or when would be the best time to add it.

F. E. Van Voris—I should like to ask Mr. Sims if he has any analytical data on these mature finishing slags. Will you tell us a little bit about that aspect of your operations.

C. E. Sims—In the basic surface-blowing operation, the slag is under the control of the operator to a considerable extent, and yet in many ways, it acts like a horse with the bit in its teeth and goes its own way. For example, if too little lime is added, the slag will attack the refractories to get CaO or MgO. If too much lime is added, an excessive amount of iron will be oxidized to flux the lime.

If not upset by last minute additions, the finishing slags tended toward a common composition containing 30 to 40 pct CaO plus MgO, 7 to 8 pct MnO (dependent on the Mn of the pig), 30 to 40 pct FeO plus Fe_2O_3 and about 8 pct silica.

Slags that were too thin gave trouble with excessive slopping, but there was also evidence that if they were too viscous they might give similar trouble. Judicious additions of lime to maintain a creamy fluid slag gave the best all-around results.

M. Tenenbaum—Mr. Sims pointed out that sulphur elimination was most rapid in the first 4 min or so of the blow, and as a partial explanation he suggested that the sulphur activity in the presence of silicon and high carbon was greater than it would be in lower carbon ranges. I think it should also be recognized that in those first 4 min there is still considerable silicon and manganese, especially manganese, present in the metal and that in the presence of this manganese the curves show that while this manganese is being eliminated, the accelerated rate of sulphur elimination is encountered. I would venture a guess that if this process were carried out with manganese-free iron, an entirely different character in the sulphur elimination picture would result.

I would like to know what disposition was made of the smaller ingots, the ones that were made in the laboratory. I also would like to know whether you feel that the cause for the slopping, this very vigorous gas evolution that you encountered during the blow, was the same as the cause of slopping in the conventional bottom-blown acid process?

C. E. Sims—No use at all was made of most of the ingots produced in the experimental work. We are convinced that the properties of a steel are more nearly a function of composition than of the manner in which it is made.

Slopping was discussed to some extent in the papers on the bottom-blown and side-blown acid processes. In summing up those discussions, it appears that, in common with the basic practice, the conditions that cause excessive slopping are those that produce a thin, watery slag. On the other hand, some crusty slags seemed to give trouble.

In some heats, there seems to be alternate periods of comparative quiescence followed by periods of explosive violence during which slag is ejected. A steady boil gives best results even though very vigorous. Blast velocities exceeding about 500 linear ft per sec also appear to give trouble with slopping.

F. L. Toy (authors' reply)—I believe that Mr. Sims, in his presentation of the paper and his answers to questions, has covered the subject very well for the present.

One question interested me particularly and that was the one regarding what effect would be had if normal Thomas molten iron of 1.8 to 2.2 pct phosphorus (as used in Great Britain and the Continent) were used in the surface-blown basic hearth. Mr. Sims gave a good answer but in addition you must consider that a molten iron of this composition would require very special measures for its production as of the immediate present in the United States. Our steel company official actually thought of using the basic bottom-blown Bessemer process in the Pittsburgh District in place of the acid Bessemer bottom-blown process in order to obtain lower phosphorus in the steel and a better application of Bessemer ingots on current orders. This, according to the best practice known for a bottom-blown basic pneumatic process, required molten iron at approximately 2 pct phosphorus. Very competent men figured the processing requirements out on through from the required burden in the blast furnace to the finished steel and the costs involved. It meant among other requirements that phosphate rock be shipped from the South. The final opinion was that the basic Bessemer process as practiced abroad would not be economical in the United States, so that a blast furnace product averaging 2 pct phosphorus would hardly appear here as an item for charge in steelmaking processes. It must be assumed, at present, that a question of using 2 pct phosphorus iron in a pneumatic process would not come up in the United States.

The question about the sulphur removal with low-manganese molten iron is a good question. Another thought, beyond the effect of manganese in removing sulphur, is one brought forth by one of our very best physical chemists, Dr. Darken, of the U. S. Steel Corp. Research Laboratory. He says that sulphur is eliminated more easily at the higher carbon (in the first part of the process) but further says that his experiments lead to the belief that a part of the sulphur is eliminated as SO_2 and goes out of the system as a gas, in the early stages when the slag is not relatively fluid.

G. R. Fitterer—I think everything has been said, but there was one thought that came to my mind, and that was that it was found in Germany that it was necessary to change the design of the large basic converters in order to have a much larger diameter to depth of bath. The erosion due to the agitated slag was decreased by this procedure. It seems to me that this would be one of the problems encountered in designing a large basic turbohearth. It is also possible that the eventual design of a large turbohearth would result in a more rectangular hearth thus allowing better impingement of the flame on the bath as well as less erosion of the banks.

C. E. Sims—Possibly it would. It may be that too deep a bath may give trouble in this process also. In our opinion, there is still very much to be learned regarding optimum design.

F. Lathe—On the question of sulphur removal, I wonder if Mr. Sims has attempted to make a sulphur balance for his converter? Did you analyze the slags for sulphur?

C. E. Sims—No, the slags were not analyzed for sulphur.

R. A. Flinn—We were very much interested in the question of catching the carbon on the way down, and the possibility of having the phosphorus correct at the same time. Comparing the European practice and your practice, you certainly improved the slope of the dephosphorization curve. Would it be possible to make it still steeper by an early ore addition or some other method to build up the oxide content of the slag early?

C. E. Sims—I cannot give you a strong opinion on that. Theoretically, an early addition of iron oxide should speed up dephosphorization unless that iron oxide reacts with the carbon and is reduced. In the heats where we did add iron oxide, the dephosphorization curve was not changed very much.

S. J. Cresswell—I am interested in the remarks concerning "catching the carbon on the way down." It is my experience that this cannot be accomplished successfully unless the blow is stopped and a steel sample taken for analysis. The Swedish Bessemer operators (acid) do attempt to catch carbon on the way down by stopping the blow and analyzing for carbon by means of a carbometer. In this country, in the production of Bessemer ingots, all heats are blown to the end point.

Attempts are made to stop the blow at various carbon contents in blowing metal for openhearth liquid metal charges.

J. L. Myer—In view of the long period which appears to be necessary to blow this converter, I was wondering if it had occurred to you that an experiment might be worth-while where the converter is tapped at the end, getting rid of all the slag and retaining about 50 pct of the metal, and then starting over, adding a half charge; in other words, a carry-over, which might do a great deal to control your processing, level out the consistency of your heats and possibly gain you some other advantages?

C. E. Sims—What do you consider is a long time?

J. L. Myer—I believe you spoke of 30 min.

C. E. Sims—Twelve minutes was the usual time on the experimental blows. Some were down to 9 min. The commercial tests were mostly on 30 tons. The shortest blowing time on them was 32 min, but there was definite evidence of too low a blast rate because the total amount of air per ton was the same as for the smaller experimental heats.

J. L. Myer—You do not visualize any advantage from that?

C. E. Sims—I do not think there would be any advantage in partial blowing and repigging as in the Talbot process for the reason that the rate of carbon drop is unabated up to the flame drop. In addition, as mentioned earlier, one would not know where to stop. On the other hand, the carbon at the flame drop is very consistent.

D. I. Brown—There is one more thing I am wondering about. The answer is going to come eventually from this group and it is quite important. With the treatment that the newspapers and radio gave the turbohearth and the reaction to the original story carried about six months ago in The Iron Age, we are going to receive a lot of questions; in fact, by Monday your customers might be on the phone saying, "We want some of that stuff." It may not be a fair question, but judging from Mr. King's remarks this process is about three years away. I wonder if anyone else here would like to make some approximation as to when he believes we will see a commercial working unit of the turbohearth type; I guess we cannot call it a pneumatic openhearth any more because Mr. Cresswell says we cannot catch the carbon on the way down, but neither does the openhearth.

C. E. Sims and F. L. Toy—The authors appreciate the opportunity to make this presentation, and wish to thank those who have contributed in the form of discussion.

Discussion — Institute of Metals Division*

New York Meeting, February 1950

The Iron-Nitrogen System (paper by V. G. Paranjpe, M. Cohen, M. B. Bever, and C. F. Floe. *Journal of Metals,* Feb. 1950, TP 2794E) 1354

The System Chromium-Carbon (paper by D. S. Bloom and N. J. Grant. *Journal of Metals,* Jan. 1950, TP 2722E) 1354

Carbides in Isothermally Transformed Chromium Steels (paper by W. Crafts and J. L. Lamont. *Journal of Metals,* Dec. 1949, TP 2709E) 1354

Carbides in Long-tempered Vanadium Steels (paper by W. Crafts and J. L. Lamont. *Journal of Metals,* March 1950, TP 2750E) 1354

A Study of the Iron-Chromium-Nickel Ternary System (paper by J. W. Pugh and J. D. Nisbet. *Journal of Metals,* Feb. 1950, TP 2785E) 1356

Faults in the Structure of Copper-Silicon Alloys (paper by C. S. Barrett. *Journal of Metals,* Jan. 1950, TP 2754E) 1358

Undercooling of Minor Liquid Phases in Binary Alloys (paper by C. C. Wang and C. S. Smith. *Journal of Metals,* Jan. 1950, TP 2756E) 1360

Measurement of Relative Interface Energies in Twin Related Crystals (paper by C. G. Dunn, F. W. Daniels, and M. J. Bolton. *Journal of Metals,* Feb. 1950, TP 2804E) 1361

Titanium Binary Alloys (paper by C. M. Craighead, O. W. Simmons, and L. W. Eastwood. *Journal of Metals,* March 1950, TP 2747E) 1363

Some Observations on the Recovery of Cold Worked Aluminum (paper by T. V. Cherian, P. Pietrokowsky, and J. E. Dorn. *Journal of Metals,* Dec. 1949, TP 2721E) 1363

Effect of Prestraining Temperatures on the Recovery of Cold Worked Aluminum (paper by T. E. Tietz, R. A. Anderson, and J. E. Dorn. *Journal of Metals,* Dec. 1949, TP 2716E) 1364

The Properties of Sand Cast Magnesium-Rare Earth Alloys (paper by T. E. Leontis. *Journal of Metals,* Dec. 1949, TP 2726E) 1366

Some Effects of Phosphorus and Nitrogen on the Properties of Low Carbon Steel (paper by G. H. Enzian. *Journal of Metals,* Feb. 1950, TP 2802E) 1366

Intergranular Parting of Brass during Anneals (paper by F. H. Wilson and E. W. Palmer. *Journal of Metals,* Dec. 1949, TP 2717E) 1366

Effect of Solute Elements on the Tensile Deformation of Copper (paper by R. S. French and W. R. Hibbard, Jr. *Journal of Metals,* Jan. 1950, TP 2755E) 1367

Electrical Resistivity and Thermoelectric Power of Antimony-Selenium Alloys (paper by B. D. Cullity, M. Telkes, and J. T. Norton. *Journal of Metals,* Jan. 1950, TP 2745E) 1367

Effects of Three Interstitial Solutes (Oxygen, Nitrogen, and Carbon) on the Mechanical Properties of High-purity, Alpha Titanium (paper by W. L. Finlay and J. A. Snyder. *Journal of Metals,* Feb. 1950, TP 2759E) 1368

A Preliminary Investigation of the Zirconium-Beryllium System by Powder Metallurgy Methods (paper by H. H. Hausner and H. S. Kalish. *Journal of Metals,* Jan. 1950, TP 2753E) 1369

Cemented Titanium Carbide (paper by J. C. Redmond and E. N. Smith. *Journal of Metals,* Dec. 1949, TP 2725E) 1371

The Elastic Coefficients of Single Crystals of Alpha Brass (paper by R. W. Fenn, Jr., W. R. Hibbard, Jr., and H. A. Lepper, Jr. *Journal of Metals,* Jan. 1950, TP 2751E) 1372

Behavior of Pores during the Sintering of Copper Compacts (paper by F. N. Rhines, C. E. Birchenall, and L. A. Hughes. *Journal of Metals,* Feb. 1950, TP 2791E) 1372

Self-diffusion in Alpha and Gamma Iron (paper by C. E. Birchenall and R. F. Mehl. *Journal of Metals,* Jan. 1950, TP 2752E) 1374

Diffusion Coefficient of Carbon in Austenite (paper by C. Wells, W. Batz, and R. F. Mehl. *Journal of Metals,* March 1950, TP 2792E) 1375

The Growth of Austenite as Related to Prior Structure (paper by A. E. Nehrenberg. *Journal of Metals,* Jan. 1950, TP 2762E) 1376

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* TP 2959E.

The Iron-Nitrogen System

by V. G. Paranjpe, M. Cohen, M. B. Bever, and C. F. Floe

DISCUSSION, R. W. E. Leiter presiding

L. D. Jaffe—The authors mention that the phase diagram in fig. 7 is a projection of the solid-phase equilibria in the temperature-pressure-concentration equilibrium diagram. This appears questionable, since all solid-phase equilibria were attained at atmospheric pressure, and not at pressures of equilibrium with nitrogen gas. Does not the iron-nitrogen diagram of fig. 7 represent the metastable equilibrium among the solid phases at atmospheric pressure, just as does the usual iron-carbon diagram (which shows cementite rather than graphite)?

V. G. Paranjpe, M. Cohen, M. B. Bever and **C. F. Floe** (authors' reply)—The iron-nitrogen phase diagram of fig. 7 represents metastable equilibrium at 1 atm. A true equilibrium diagram at 1 atm pressure shows only the solubility lines[18] of nitrogen (gas) in α and γ iron. Increasing pressures of nitrogen brings about a change in the nature and composition of phases in mutual equilibrium as shown by recent experiments[19] where the γ' phase was produced at 450°C by nitrogenizing with nitrogen under 2700 atm pressure. It is thus possible, at least in principle, to construct an equilibrium diagram with temperature, pressure and composition plotted along the three axes. If the effect of simple hydrostatic pressure on the solid phases is negligible, one can project the lines of solid-solid phase solubilities on to a temperature-concentration plane. Fig. 7 would be such a projection.

The phase diagram of fig. 7 is similar to the iron-cementite diagram since both represent metastable conditions, the nitrides tending to evolve nitrogen gas and the cementite tending to form graphite.

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[18] A. Sieverts: *Ztsch. Phys. Chem.* (1931) **155A**, 299.

[19] Krichevskii and Khazanova: *Journal* Phys. Chem. (USSR) (1945) **19**, 676.

L. D. JAFFE, Watertown Arsenal, Watertown, Mass.

The System Chromium-Carbon

by D. S. Bloom and N. J. Grant

DISCUSSION, G. M. Cover presiding

F. R. Morral—The cubic chromic carbide (Cr_4C) was probably first recognized by Moissan.[4] From such a formula and other considerations, one would expect a total of 120 atoms in the unit cell; however, only 116 atoms of metal and carbon atoms could be made to fit into the lattice of the compound as measured on X-ray diffraction patterns.[11] Although the formula Cr_4C may be simpler, the $Cr_{23}C_6$ appears to be more representative for this compound, and is generally being used.[12]

N. J. Grant and D. S. Bloom (authors' reply)—We are well aware that $Cr_{23}C_6$ is correct and so noted in the text. However we were possibly guilty of laziness in continuing to use the easier but incorrect designation Cr_4C.

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[11] A. Westgren: Jernkontorets Ann. (1933) 501-502.

[12] H. J. Goldschmidt: Iron and Steel Institute (1948) **160**, 345; (1949) **163**, 385; *Metallurgia.* (1949) **40**, 103.

F. R. MORRAL, Syracuse University, Syracuse, N. Y.

Carbides in Isothermally Transformed Chromium Steels

by W. Crafts and J. L. Lamont

DISCUSSION, G. M. Cover presiding

F. R. Morral—I note an unidentified constituent in table V of this interesting paper. Goldschmidt[4] has indicated the presence of a new carbide in chromium steels. This has 8.7 to 9.4 pct C and a lattice reminiscent of austenite with a parameter of $a = 3.611$ kx. I wonder if the authors have considered this possibility for their constituent. Some years ago in the iron-rich Fe-Al-C system a constituent was identified whose pattern was similar to that of austenite. The edge of the unit cell was found to be 3.75Å. The carbon content was about 4 pct.[5]

W. Crafts and J. L. Lamont (authors' reply)—The possibility suggested by Professor Morral that the unidentified constituent is the austenite-like carbide described by Goldschmidt was considered, but the pattern suggests a lower order of symmetry than the cubic austenite-like structure.

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[4] Goldschmidt: *Nature.* (1948) **162**, 855.

[5] F. R. Morral: Iron and Steel Institute. (1934) **130**, 419.

F. R. MORRAL, Syracuse University, Syracuse, N. Y.

Carbides in Long-tempered Vanadium Steels

by W. Crafts and J. L. Lamont

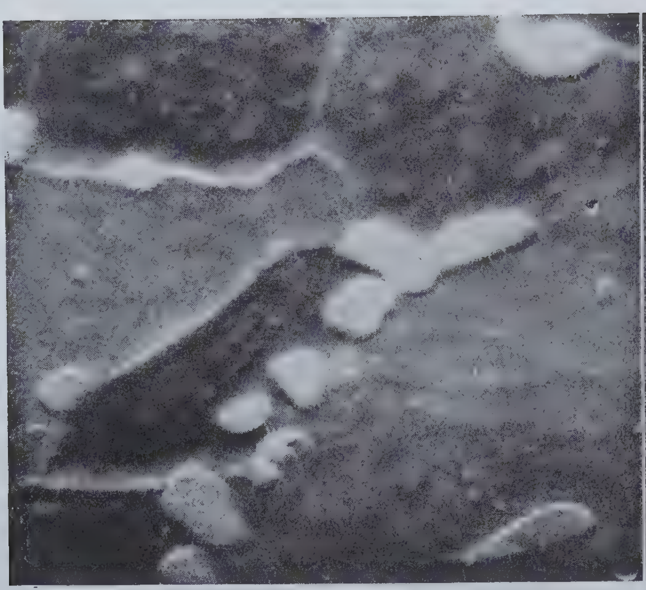
DISCUSSION, G. M. Cover presiding

P. Coheur and L. Habraken—We read this paper with great interest and are glad to congratulate the authors for their valuable work, supplying an important contribution to the mechanism of tempering on the carbides in vanadium steels. We are in a good position to appreciate this work since we have been studying, for more than a year, Cr-Mo steels of a composition similar, but less highly alloyed (namely 0.1 pct C, 3 pct Cr, 1 pct Mo).

Our results are quite in concordance with the authors', however, we wish to point out that it is very interesting to use equally the electron microscope in order to observe the variations of microstructure in steels. We have studied simultaneously the evolution of the carbides *in situ* with the electron microscope, and, after extraction, again with the electron microscope, and then with X-rays.

The first results which we have obtained have been communicated at the Congress of Delft (July 1949) and at the "Journées de la Métallurgie" in Paris (October 1949). These may be summarized as follows:

After tempering with varying either the tempering temperatures or the tempering times, the carbides show two evolutions. The first one is connected to the carbides existing in the steels, principally in the boundaries of the grains. For some groups of steels these carbides may coalesce and for other groups they may



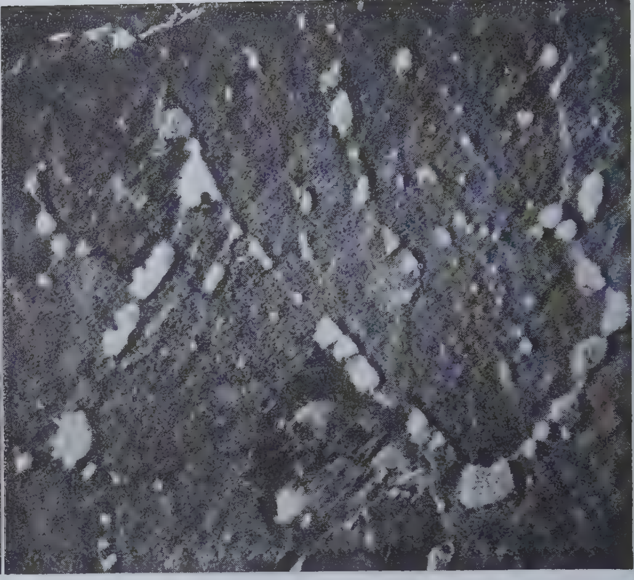
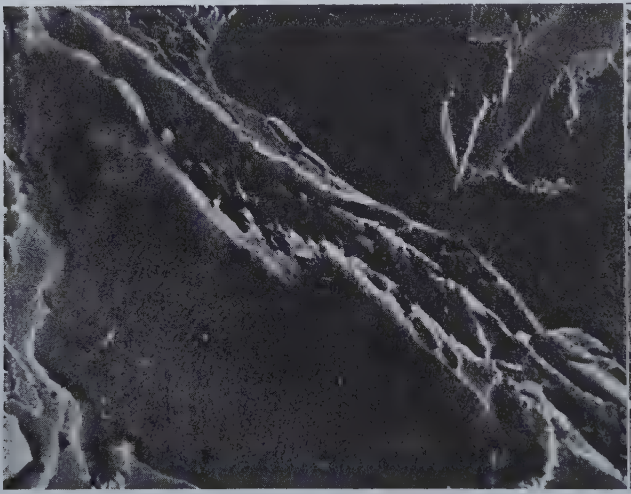


Fig. 12 (left)—Cr-Mo steel as quenched from 775°C showing grain boundary carbides. X12,000.

Fig. 13 (right)—Same as fig. 12 after 60 hr tempering. X12,000.



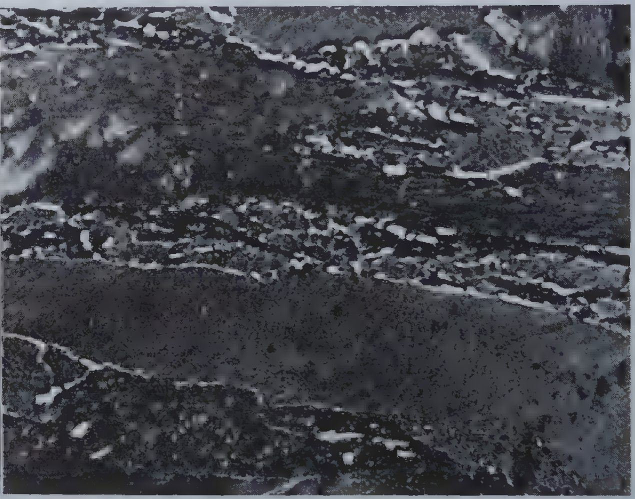


Fig. 14 (left)—Same as fig. 12 showing carbides in bainite needles. X25,000.

Fig. 15 (right)—Same as fig. 14 after 60 hr tempering. X25,000.

decrease in volume, and in this latter case, we can see with X-rays a new phase. Figs. 12 and 13 illustrate this variation. Fig. 12 refers to the original steel and fig. 13 after a 60 hr tempering.

The second evolution takes place in the bainite needles. In the course of tempering, we have observed precipitates which appear, then coalesce. Figs. 14 and 15 illustrate this variation: fig. 14 refers to the original state prior to tempering and fig. 15 after 60 hr tempering.

In the case of the steel referred to in the foregoing figures, we should like to state that the steel has been heated to 775°C for 6 hr, then tempered at 550°C. We observed that, after some time, the proportion of the carbide type M_6C—probably $(Fe, Cr)_4Mo_2C$—to carbide $(Fe, Cr, Mo)_{23}C_6$ changes, the latter increasing during the tempering process.

The presence of these two principal carbides is in fair agreement with the conclusions of the authors; however it is interesting to notice that tempering at a lower temperature modifies the ratio in the precipitated carbides.

The observation with the electron microscope of the carbides *in situ* and after extraction, induces us to think that the type M_6C appears preferentially in the bainite needles, while the carbides $Cr_{23}C_6$ occurs more frequently in the grain boundaries. Therefore, we think many benefits may be derived from conjugating several investigation methods in the study of this very complicated phenomenon.

W. Crafts and J. L. Lamont (authors' reply)—The suggestion of Messrs. Coheur and Habraken that carbides be investigated *in situ* by electron micrographs of replicas as well as after extraction has much value and should assist in the understanding of the tempering process. In a limited examination of this type we have not observed the specific grain boundary behavior described in their discussion but feel that the subject has not been exhausted.

P. COHEUR and L. HABRAKEN, Centre National de Recherches Métallurgiques, Liège, France.

A Study of the Iron-Chromium-Nickel Ternary System

by J. W. Pugh and J. D. Nisbet

DISCUSSION, F. H. Wilson presiding

F. B. Foley—The use of data published by Wever and Jellinghaus in 1931 to fix boundaries of the sigma phase in the Fe-Cr system, in the face of the author's own references to the suggestions of Bradley and Goldschmidt, Aborn and Bain, and Hougardy that the phase is much more extensive, and the very much more accurate work, which weighs heavily in favor of these suggestions, of Cook and Jones, published in 1943 and evidently disregarded by the authors, makes their derived ternary diagram, especially fig. 15 for 400°C, quite inaccurate on the Fe-Cr side and affects the extent of phase boundaries in the most controversial and important part of this ternary system. In commercial Fe-Ni-Cr alloys the occurrence of sigma has been observed time and time again at lower chromium contents than that of the 24 pct Cr, 16 pct Ni, 60 pct Fe alloy which is the lowest permitted by fig. 15 of practically carbonless metal. Newell reports sigma in 27 pct Cr-Fe even with some carbon present to be one of the greatest detriments to its extensive application, whereas Pugh and Nisbet set a low limit of 36 pct Cr for sigma in the binary Fe-Cr system.

J. J. Heger—The diagrams presented by the authors do not agree with observations made on commercial Fe-Cr and Fe-Cr-Ni alloys, nor do they agree with two recent investigations made on the Fe-Cr and the Fe-Cr-Fe systems.

I refer first to the investigation made by Cook and Jones[16] on the sigma region of the Fe-Cr system. On the basis of their results which were published in 1943, Cook and Jones established new boundary limits for the sigma and the alpha plus sigma regions. These new limits have been accepted and are incorporated in the Fe-Cr diagram that appears in the 1948 edition of the Metals Handbook. This diagram is shown here as fig. 34.

As will be noted, the boundary limits of the alpha plus sigma region in this diagram extend to much lower chromium contents than do those in the diagram presented by the authors in fig. 2. These new limits indicate that sigma phase should form in an Fe-Cr alloy containing 26 pct Cr, and experience with commercial alloys confirms this finding. Indeed, recent studies on a commercial Fe-Cr alloy containing 17 pct Cr have shown sigma phase to be stable in this alloy at 550°C.

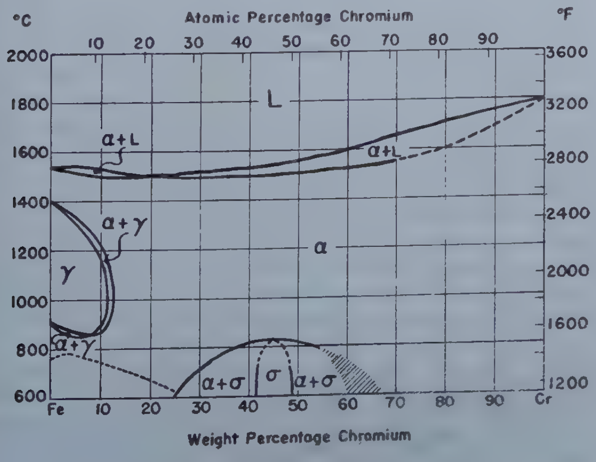


Fig. 34—Fe-Cr diagram.

I recognize that the authors' work did not include studies on the sigma region; however, I believe this is a serious omission because sigma phase may profoundly affect the physical properties of these alloys and should be evaluated in any investigation which attempts to relate physical properties to the equilibrium diagram.

The second investigation to which I refer is that made on the Fe-Cr-Ni system by Rees, Burns, and Cook,[17] who used pure alloys and employed heating times that extend to 200 days. These investigators published their results in July 1949 and from these results constructed isothermal sections at 800° and 650°C. The isothermal section at 650°C is shown here as fig. 35. This diagram indicates sigma phase should form in a pure 18 pct Cr-8 pct Ni alloy. Although sigma phase has not been observed after 10,000 hr at 1200°F in commercial 18-8 alloys containing carbon and nitrogen, it has been observed under the same conditions in 18-8 alloys modified with titanium and columbium, both of which serve to reduce the effect of carbon and nitrogen.

This section and the one at 800°C suggest that the constant iron sections which are presented by the authors, should be considerably altered, if they are to represent an accurate picture of the system. A few of the suggested alterations are as follows:

In fig. 9, the section at 50 pct Fe, the gamma plus sigma region should be widened, not narrowed at 800° and 650°C.

In fig. 10, the section at 60 pct Fe, the gamma plus sigma region should be widened at 800° and 650°C.

In fig. 11, the section at 70 pct Fe, an alpha plus sigma, an alpha plus gamma plus sigma, and a gamma plus sigma region should be added.

In fig. 12, the section at 80 pct Fe, the alpha plus gamma region should be widened at 800°C.

In fig. 13, the section at 90 pct Fe, the alpha plus gamma region should be widened at 650° and 800°C.

Undoubtedly, the chief reason for the discrepancies between the authors' data and those of Rees, Burns, and Cook is that the authors did not employ long enough heating times to allow for transformation. In this connection, I wish to warn that transformations in these alloys, particularly transformations at temperatures below 800°C, are extremely sluggish and may require a year or more to approach completion. Therefore, unless extremely long heating times are employed or steps are taken to accelerate these transformations by such means as mechanical working, the results will not yield an accurate picture of the alloy system. Certainly, an accurate picture is needed for the development of better high-temperature materials.

E. J. Dulis—The purpose of this work is not clear. If an improvement of the ternary equilibrium diagram of the Fe-Cr-Ni system was wanted, it seems logical that testing techniques superior to those previously used would be a prime requirement. To approach equilibrium in this system, long holding times are needed; a fact established long ago but apparently ignored by the present authors, who used the continuous heating and cooling tests in equilibrium studies. A publication on the same system by Bradley and Goldschmidt[5] was criticized by Monypenny in a

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[16] A. J. Cook and F. W. Jones: *Journal* Iron and Steel Institute. (1943) No. II, p. 217.

[17] W. P. Rees, B. D. Burns, and A. J. Cook: *Journal* Iron and Steel Institute. (July 1949) 162, Part 3, p. 325.

F. B. FOLEY, International Nickel Co., Bayonne, N. J.; J. J. HEGER, Carnegie-Illinois Steel Corp., Pittsburgh, Pa.; E. J. DULIS, U. S. Steel Corp., Kearny, N. J.; S. J. ROSENBERG, National Bureau of Standards, Washington, D. C.

discussion of the work as not "being in anyway an advance on existing knowledge," because the times to establish equilibrium were not long enough. It is unfortunate that the present authors did not benefit by mistakes made in the past.

Other points meriting specific comment are:

The use of dilatometer and electrical measurements on relatively rapid heating and cooling, and hardness tests after cooling from various temperatures (the holding times of which are not given), are not sensitive tools for equilibrium studies of this system.

Micrographs of specimens quenched from 2100°F would give information about an isothermal section at that temperature only. Throughout the paper, implications are made that the micrographs indicate phase boundaries at lower temperatures.

The comprehensive study on the Fe-Cr system which the authors believe is needed has, as pointed out by Messrs. Foley and Heger, been made by Cook and Jones.[16]

The correction of the work of Schafmeister and Ergang on the constant iron plane of 50 pct Fe (fig. 9) is very questionable. The gamma plus sigma and gamma boundary found by the earlier investigators by X-ray diffraction, magnetic, microscopic, and hardness tests, was based on holding times up to 1000 hr at 650° and 800°C. As the points of the present authors are based on hardness tests only, for alloys of unknown time at temperature, it seems more logical to accept the earlier work as being correct. The supposed micrographic substantiation, figs. 28 and 30, fails to show anything about the lower temperature ranges, as pointed out above.

Differences between the work of Schafmeister and Ergang and that of the present authors for the 70 pct Fe plane are quite marked. The absence of regions containing sigma in the present work is probably due to insufficient holding times.

With reference to fig. 15, no isothermal work was performed in any of the four references cited on this system involving the sigma phase at 400°C. Where did the present authors get the isothermal diagram at the 400°C level?

In the summary the authors mention an enlargement of the gamma phase at 60 pct Fe, but in the text (p. 273) it is stated that the agreement of the present and earlier work for this alloy is good, as shown in fig. 10. Do the authors mean 50 rather than 60 pct Fe?

S. J. Rosenberg—One of the current projects at the National Bureau of Standards involves a study of the solubility of carbon in 18 pct Cr-10 pct Ni austenite. In connection with this study, several high-purity alloys of iron, chromium, and nickel, containing various amounts of carbon were prepared by melting and solidifying under vacuum. It is interesting to compare some of our data with information furnished by the authors.

Of particular interest to us is the Fe-Cr-Ni isothermal section at 1100°C, presented as fig. 16 of the paper. According to this diagram, our base alloys should have been completely austenitic on quenching from this temperature level, an expectation which was not realized.

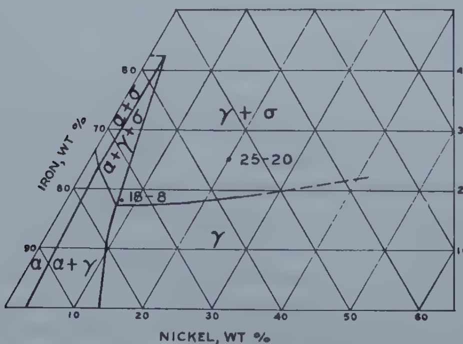


Fig. 35—650°C Isothermal section of Fe-Ni-Cr diagram.

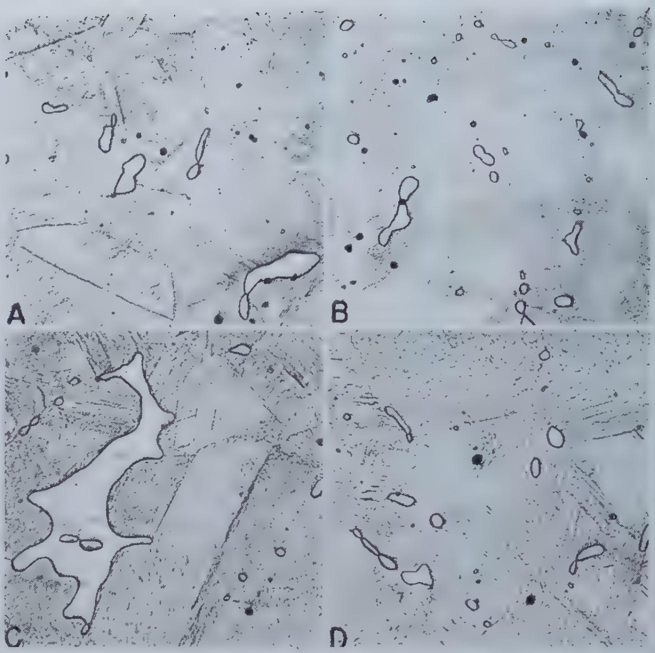


Fig. 36—Microstructure of alloys showing ferrite as quenched from 1080°C.

Our alloys were quench annealed from 1080°C, which is fairly close to 1100°C, and all of our low-carbon alloys contained delta ferrite after this treatment. Four alloys were prepared without any carbon additions; their analyses are given in table I.

Table I. Analyses of Alloys

Alloy No.	C	Mn	P	S	Si	Cr	Ni	O_2	N_2	H_2
2	0.016	0.04	0.002	0.021	0.060	17.46	10.01	0.023_5	0.008_5	0.0001_2
3	0.007	0.01	0.001	0.009	0.010	17.51	10.25	0.025_7	0.001_8	0.0003_3
4	0.013	0.01	0.001	0.008	0.003	18.26	9.90	0.002_6	0.001_6	0.0004_3
9	0.012	0.01	0.001	0.008	0.004	16.80	10.30	0.003_3	0.001_3	0.0005_7

It will be noted that all of these alloys contained less than 0.02 pct C, the amount listed by the authors as an impurity in their alloys. Since carbon promotes the formation of austenite, it follows that if ferrite is present in Fe-Cr-Ni alloys containing small amounts of carbon as an impurity, carbon-free alloys should contain even more ferrite. The microstructures of these four alloys after quenching from 1080°C is shown in fig. 36.

It may be argued that only austenite was present at the quenching temperature and that the ferrite observed formed during the quenching. The sluggish nature of the transformations in these alloys is so well known, however, that this seems to be an unlikely explanation. It is more reasonable to believe that the structures observed are representative of the alloys at the temperature noted.

Although the isothermal section at 1100°C (fig. 16) was apparently constructed from the work of the several references cited by the authors, the impression is gathered that they check this diagram. Our evidence supports the belief that this diagram is in error and that the gamma field is considerably more restricted at the iron corner than appears from the diagram.

J. W. Pugh and **J. D. Nisbet** (authors' reply)—We wish to thank the discussers for their comments on this paper.

The objection which several of these gentlemen make to the use of phase diagrams which show the sigma region considerably more restricted than recent investigators have found it may be answered in several ways. Although the importance of sigma in this system is recognized, none of the experimental work was calculated to reveal sigma, if it was too sluggish to develop in the experimental time employed, nor did the formation of sigma ever take place to affect the results. At the time the paper was prepared the recent work of Rees, Burns, and Cook[17] on the ternary sigma had not been published. Several investigators, as pointed out, had shown the Fe-Cr binary sigma to be more extensive than the diagram of Wever and Jellinghaus, but the binary diagram which fits the ternary was used in the interest of consistency.

To answer Mr. Dulis specifically, it must be repeated that the authors were abundantly aware that the formation of sigma would not take place as a result of the treatments given those alloys which might contain this phase. His assertion is untrue that micrographs taken of alloys quenched from one temperature were implied to indicate phase boundaries at another temperature. The micrographs of figs. 28 and 30 give evidence about the phase situation at 1100° and were obviously not implied to show anything about lower temperature ranges. Fig. 15 which shows an isothermal section of the diagram at 400°C was taken from published pseudobinary systems. It is the 50 pct Fe section, as pointed out by Mr. Dulis, which disagrees with the data of this investigation.

Mr. Rosenberg's observation of ferrite in an 18 pct Cr-10 pct Ni alloy is interesting. Fig. 23 (20Cr-10Ni), a micrograph of an alloy which is yet closer to the phase boundary than this alloy, shows no evidence of ferrite after holding 15 hr at 1100°C. It is very improbable that the ferrite evident in Mr. Rosenberg's micrographs could have formed during quenching.

Mr. Foley pointed out that: "In commercial Fe-Ni-Cr alloys the occurrence of sigma has been observed time and time again at lower chromium contents than that of the 24 pct Cr, 16 pct Ni, 60 pct Fe alloy which is the lowest permitted by fig. 15 of practically carbonless metal." Such a composition as that mentioned by Mr. Foley does not exist in commercial alloys, because commercial alloys contain extraneous elements and products of deoxidation which often amount to 1 to 2 pct of the total composition. It is reasonable to expect, therefore, that sigma might exist in an alloy containing 24 pct Cr, 16 pct Ni, 2 pct of Si, Mn, P, S, C, O, N, and 58 pct Ni. Such a commercial alloy is far removed from the Fe-Cr-Ni ternary system when the low solubility of these extraneous elements is taken into account. Therefore, would not one expect a phase other than the f.c.c. ternary solution?

We believe the discussion of this paper has brought out an important point: The real Fe-Cr-Ni ternary phase diagram cannot be used without considerable discretion in its interpretation for evaluating phases which might exist in commercial alloys.

Faults in the Structure of Copper-Silicon Alloys

by C. S. Barrett

DISCUSSION, F. H. Wilson presiding

W. Hofmann, J. Ziegler, and **H. Hanemann**—Having dealt with the same alloys in the winter 1941 to 1942, we want to give a short report on the generating of the hexagonal kappa phase by deforming the supersaturated alpha phase, which we then observed. This work was delivered as a Doctor of Engineering dissertation to the Technical University of Berlin by J. Ziegler in 1942. It still exists in two copies, somewhat damaged, a brief publication of it having been issued in Fiat-Review.[29]

Our work was started from the alloy Tombasil with 4.5 to 5 pct Si, 14.5 to 14 pct Zn, the rest Cu. Torpedo propellers were die cast from this alloy in Germany during the war. In order to improve this alloy, annealing was tried. By this treatment the alloy became at the same time harder and more brittle. A further research of this process was made in the Göttingen University[30] and the "Institut für Metallkunde" of the Technical University of Berlin. It soon was apparent that the Cu-Si diagram at our disposal[15, 31, 32] would not fit the observations. For this reason the pith of the matter became from then on the Cu-Si system. At that time we did not know of Smith's[12] and Andersen's[13] latest diagrams. We first knew of them from Dr. Barrett's publication.

Twenty-two alloys containing 2 to 11 pct Si were melted in a nitrogen atmosphere and generally homogenized for 2 to 4 hr at 800°C. Part of the samples were then annealed at 700°, 600° and 500°. Annealing was followed by quenching in water. The phases corresponding to the various temperatures were identified by X-ray and microscopy. The Debye-Scherrer photographs generally were made of filings. The latter were produced after the last anneal of the samples, then equally annealed another 30 min in evacuated glass tubes and quenched in water.

In the region of concentrations examined, the Cu-Si phases already known to us were observed:

alpha, kappa (then called beta by us), gamma.

By hot exposing an alloy of 7.69 pct Si at 800° and 750°,

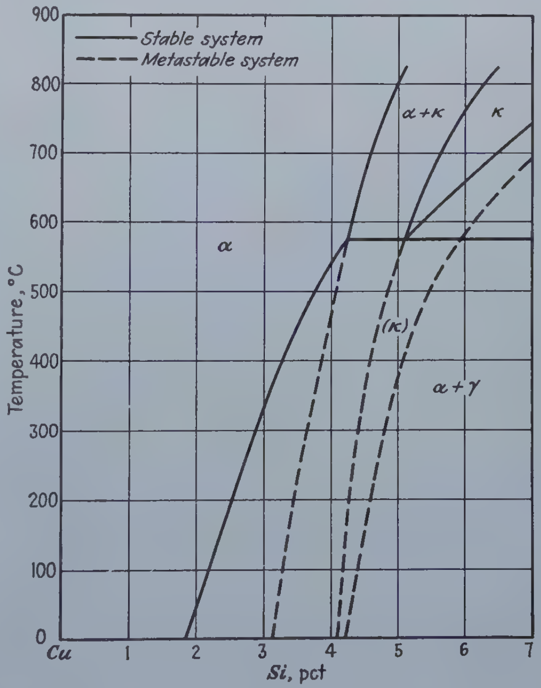
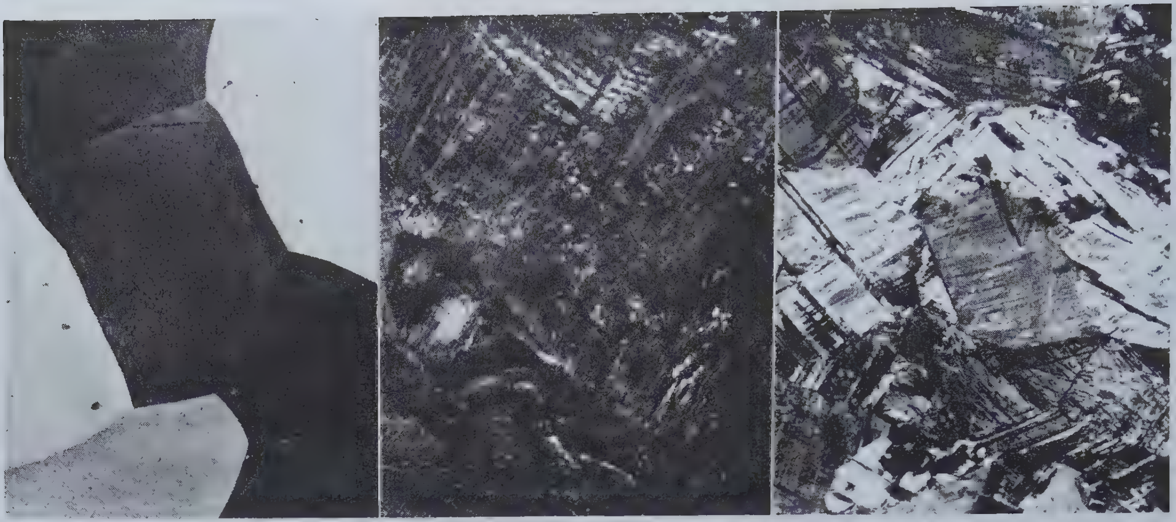


Fig. 17—Schematic diagram of copper-silicon. Solid lines: stable system, dotted lines: metastable system.

W. HOFMANN, Technische Hochschule Braunschweig, Braunschweig, Germany; J. ZIEGLER, Metallurgist; H. HANEMANN, Technische Hochschule Berlin, Berlin, Germany.



Figs. 18 to 20—Alloys homogenized 4 hr at 800°C and quenched. Nonetched microsections. Exposures in the polarized light. X150

Fig. 18 (top)—5.63 pct Si. Alloy quenched after homogenizing at 800°C from 700°C (5 hr). Pure kappa.

Fig. 19 (center)—4 pct Si. X-ray diagram of the filings shows only alpha though microsection anisotropic.

Fig. 20 (right)—4.5 pct Si.

there appeared, in addition to kappa, a phase, the structure of which we could not determine. We considered it as the delta phase. It could not be quenched. In its place gamma lines appeared at room temperature. All these observations are in agreement with Smith's[12] publication, unknown to us at that time. There is a further agreement in the fact that kappa decomposes into alpha and gamma below 600° and that this eutectoid decomposition can be prevented by quenching. The eutectoid could not be proved by dilatometer observations. We explained this by the minute change of volume which this transformation caused. Dr. Barrett's treatments confirm this explanation. We then constructed the diagram reproduced in fig. 17. Its lines were drawn to correspond to equilibrium. It is true that this diagram does not quite come up to the accurateness of Smith's.

The microscopic examination was almost entirely carried through with nonetched microsections in polarized light. Here kappa shows large homogeneous crystals which cause strong effects in the polarized light (fig. 18). Alpha has a tendency to form twins and slip bands. It is remarkable that in alloys which contain the two phases together, alpha and kappa cannot be distinguished from each other. We only observed an optic anisotropy increasing with the kappa content, and vice-versa, slip bands and twins increasing with the alpha content. Alpha and kappa seemed to penetrate one another completely without visible grain boundaries. We were surprised to observe an effect in the polarized light even in alloys which in the Debye-Scherrer-diagram of filings proved as pure alpha or alpha with little beta (figs. 19 and 20). Similar observations in the polarized light had been made previously by M. von Schwarz.[33] He had referred the optic anisotropy to stresses in the lattice of the alpha phase or to segregations from the supersaturated alpha phase. From the fact that the microsection of an alloy, which in the X-ray diagram of filings consisted of cubic phases (alpha and gamma), appeared anisotropic in the polarized light, we concluded that kappa might be built as a metastable phase in lower temperatures. Apparently it was generated by the deformation in grinding the samples which originally contained alpha. In order to prove this a number of tests was carried through.

A sample with 4.45 pct Si had been homogenized,

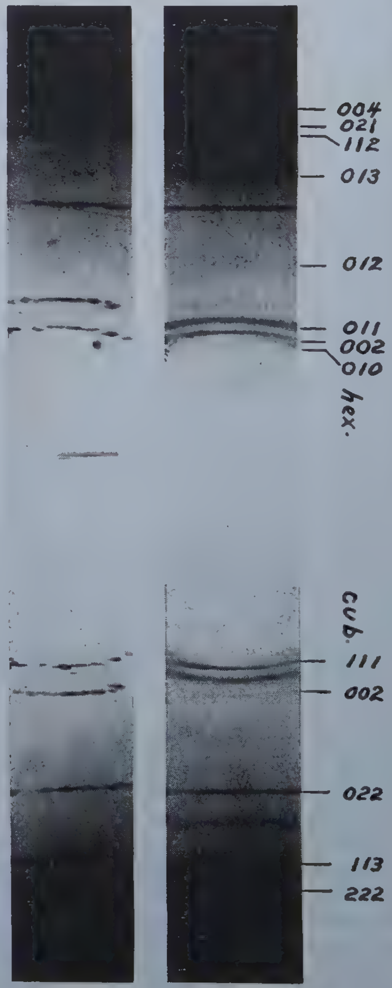


Fig. 21 and 22—Debye-diagrams. Alloy with 4.45 pct Si rod-formed. Fig. 21 (left)—Sample homogenized and quenched: alpha. Fig. 22 (right)—Same as fig. 21 forged and annealed 3 hr at 300°C: alpha plus kappa.

quenched and then X-rayed. The pattern showed only alpha (fig. 21). After forging the rod, the X-ray diagram now showed kappa lines beside alpha. By annealing the sample at 300° after deformation the kappa lines became even sharper (fig. 22).

The alloy with 5.12 pct Si was exposed to similar tests. Here the homogenized and quenched rod showed the same lines (alpha and kappa) as the sample after deformation. By annealing the rod at 300° for 3 hr, the intensity of the kappa lines increased at the cost of the alpha lines. After a two days' further annealing at 500°, alpha besides a little gamma appeared in the X-ray diagram. These phases correspond to the equilibrium. This last specimen was very carefully ground and polished, and the superficial layer, deformed by grinding, was etched off. Thus the anisotropy in the polarized light ceased. As the face-centered cubic alpha phase and the hexagonal close-packed kappa phase differed from one another only by the stacking of atomic planes, we—just as Dr. Barrett does—referred to the transformation of the deformed alloy as a translation mechanism, similar to the cobalt transformation. Furthermore we believed that we could explain the transformation of the supersaturated alpha phase into alpha plus kappa by a metastable diagram, as represented in fig. 17 by dotted lines. If this explanation be correct, proof should be given that the silicon content of the supersaturated alpha phase is lowered to the value of the dotted line when generating kappa by deformation.

Finally an observation made in the pattern of fig. 22 should be mentioned. Here the kappa lines are broadened while the alpha lines, in spite of the deformation, have remained sharp. From this it follows that the broadening of the kappa lines is not due to deformation but to the small thickness of the hexagonal close-packed lamellae. Having found our results by methods somewhat different from Dr. Barrett's, we believe that one work is a good supplement of the other one.

Dr. Barrett's X-ray methods mean a progress compared with ours, as the faults caused by deformation of the copper-silicon alloys are now analyzed in detail.

C. S. Barrett (author's reply)—The information from the independent investigation in Berlin confirms a number of conclusions of the present paper and of earlier studies of these alloys. The discussers' conclusion that kappa, not gamma′, is generated by cold work appears at first contradictory but can readily be reconciled with the present results. The conclusion was based on broad lines in Debye patterns, which coincided with the position of kappa lines; but with the higher resolution possible in our oscillating patterns of gamma′, as in fig. 8, it is seen that several kappa lines are flanked by a pair of gamma′ maxima, one on each side of the true kappa line. Failure to resolve these satellite lines around the kappa lines 10·1, 10·3, and 20·3 would naturally lead to the conclusion that kappa was generated. The discussers' Debye pattern for a 4.45 pct Si alloy forged and annealed at 300°C shows 10·1 and 10·3 lines to be broader than 00·2; this is in accord with the idea that unresolved satellites are present and could not be accounted for, incidentally, by the theory of thinness of hexagonal lamellae proposed by the discussers. Lamellae that are thin in the c dimension would have given a pattern in which 00·2 is also broadened.

The observation of optical anisotropy in unetched microsections need not require the conclusion that the strains of grinding and polishing generate kappa. The gamma′ and faulted alpha phases that are left after such straining are, presumably, both anisotropic.

References

[29] M. Hansen: *Fiat Review of German Science.* German edition. Vol. 31, p. 95.

[30] G. Masing and H. J. Wallbaum: *Ztsch. f. Metallkunde.* (1942) **34**, 87-89.

[31] C. S. Smith: *Journal* Institute of Metals. (London) (1928) **40**, 359-371.

[32] C. S. Smith: *Trans.* AIME (1929) **83**, 414-439.

[33] M. von Schwarz: *Ztsch. f. Metallkunde.* (1932) **24**, 97.

Undercooling of Minor Liquid Phases in Binary Alloys

by C. Wang and C. S. Smith

DISCUSSION, F. H. Wilson presiding

D. Turnbull—In the opinion of the writer the most interesting result described in this paper is that the distribution of tin with respect to solidification temperature has several fairly well-defined maxima. It appears that each peak may be associated with a catalytic impurity of some rather specific composition.

Recently we have obtained some additional evidence in favor of this viewpoint in experiments on the supercooling of lead droplets coated with different surface films. The distribution of lead droplets, ostensibly coated with lead sulphate, with respect to solidification temperature exhibited two distinct and reproducible maxima, one at 20° supercooling and the other at 47°. On the other hand, when the droplets were ostensibly coated with halide films, no solidification was perceptible until the aggregate was supercooled more than 55°. Upon further cooling a single well-defined peak centering at 60° supercooling was observed. Since the particle size distribution was the same in these two sets of experiments it appears that the most reasonable interpretation of the results is that the sulphate surface film or its reaction products with lead are much more effective in catalyzing the nucleation of lead crystals than are lead halide films.

C. S. Smith (authors' reply)—Dr. Turnbull's experiments with lead drops coated with various surface films are most interesting. However, before drawing conclusions from the cooling curves described in the paper as to the existence of a few nucleus types effective at a few different temperatures, one must consider the state of subdivision of the liquid metal. In the Al-Sn alloy used, the tin was not in uniform droplets but tended to collect in three distinct shapes—in long interconnecting prisms along grain edges, in somewhat elongated interdendritic branching pools, and in isolated droplets. A single nucleus will solidify only the metal in contact with it, and the heat evolved will be proportional to the connected volume. A uniform distribution of nuclei of random effectiveness in such an alloy will cause peaks on the specific heat curve on cooling, which correspond to the volume distribution of tin and tell nothing about the nucleus type. In any real alloy both effects will be combined, and it seems impossible at present to distinguish between them.

M. B. Bever—The thesis of this interesting paper is supported by a combination of positive and negative evidence. The authors have shown that under certain conditions a liquid phase may undercool, if it is dispersed in a thoroughly discontinuous manner throughout a solid matrix. They also found that undercooling

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failed to take place in two systems in which the liquid phases were continuous. The authors' interpretation of these results concentrates on this difference in geometrical distribution. The argument is convincing although the evidence is limited to very few alloy systems.

The question arises as to whether in addition to the effect of distribution there is also an interaction between the matrix and the liquid. The paper suggests that solid copper may nucleate the solidification of a lead-rich or bismuth-rich liquid. One may wonder whether this nucleation is affected by specific properties of the phases in a given system.

It is probable that a solid matrix interacts with a dispersed solid phase. The retention of gamma iron in a Cu-Fe alloy mentioned in the paper may be explainable by such solid-to-solid interaction rather than by the lack of a nucleating effect: stresses, perhaps aided by forces of registry or coherency, may be expected to stabilize dispersed particles of face-centered iron in copper.

This extensive application of the method of thermal analysis first suggested by Dr. Smith some years ago is of interest on its own account. However, the numerical results for the heat of fusion of tin raise a question. The authors report values ranging from 15.4 to 16.3 for the total heat evolution due to tin solidification, while the generally accepted value is in the range of 14.2 to 14.5 cal per g of tin. Because of the magnitude of this discrepancy and the range of values found by the authors, a clarification of this point would be desirable, as it may have a bearing on the interpretation of the undercooling phenomena or on the accuracy of the method of thermal analysis.

C. S. Smith—Dr. Bever's comments are appreciated. In regard to the nucleation of a solid phase from another solid it seems probable that Dr. Bever's solid-solid interaction can be treated in terms of interfacial energy as Turnbull[6] has indicated for the solid-liquid case. Interface energy is the result of strain energy as well as chemical interaction energies, etc., and can serve as an approximate inverse index of ease of nucleation.

Dr. Bever questions the accuracy of the thermal analysis method used. At least half of the difference between the observed latent heat and the commonly accepted value for pure tin is due to the fact that the tin-rich phase in the aluminum alloys is actually a eutectic containing about 0.5 pct Al by weight. Since aluminum has a latent heat of solidification of about 95 cal per g, the eutectic would be expected to have a latent heat of about 0.5 cal above that of pure tin. The cooling curve method certainly does not have the absolute accuracy of Syke's method or others using quantitative electrical heat input measurements; it does, however, have the virtue of extreme simplicity and cheapness and of being applicable to cooling. If sufficient care is taken it will give results of quite acceptable precision. The initial measurements on beta brass, described in the 1940 paper,[5] gave specific heat measurements accurate to within about 2 pct. The integrated area corresponding to an arrest spread over a wide temperature range would not be so accurate. It should be remembered that the latent heat of solidification of tin in the present experiment represents only a small fraction of the total heat effect being measured, and an error of 5 pct is not surprising, since no attempt was made to achieve high accuracy. The most likely source of error lies in the fact that the constants of the thermal resistor were obtained by using a copper standard, whose thermal characteristics would undoubtedly be slightly different from those of the aluminum alloys.

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[6] D. Turnbull: Principles of Solidification. Thermodynamics in Physical Metallurgy. A.S.M. (1950) 287-306.

Measurement of Relative Interface Energies in Twin Related Crystals

by C. G. Dunn, F. W. Daniels, and M. J. Bolton

DISCUSSION, G. P. Halliwell presiding

J. P. Nielsen—The data that Dr. Dunn and his associates have been obtaining are welcome checks on the theoretical aspects of grain boundary energies. With reference to the comments on the validity of the interfacial tension concept, I should like to say that I have been having considerable difficulty myself in untangling the confusion between "interfacial tension" and "interfacial energy." The confusion however resolved itself for me when I learned that "interfacial tension" for solids, or at least crystals, is used with two distinct meanings.

One meaning[12, 13] that is implied for "interfacial tension" is the work necessary to produce or increase the surface of the solid in question by a unit area, temperature and pressure held constant. This comes from the somewhat surprising but simple fact that surface tension and surface energy in the case of liquids are identical quantities. This synonymity has carried over to crystals, where it should be kept in mind that the tension connotation has meaning only by analogy with liquids and that no real stresses are being referred to. The only reason that there is apparently a set of stresses acting at a grain boundary junction is the optical illusion that liquid interfaces are being observed for the grain boundaries.

The other meaning[8, 14, 15] for the term has to do with actual states of stress in the surface of a material as would be measured by a system of forces applied to the surface to equate the surface stress state with that in the body of the crystal.

J. B. Hess—Since the authors have proposed that the surface tension concept should be discarded in order to deal with the general case of interface energies in solids, their attention should be called to a recent paper by Gurney.[16] The latter has shown, from a thermodynamic argument, that surface tension is a valid concept in solids. In fact, Gurney has rejected the idea that surface tensions are merely mathematical fiction and, instead, has given an interpretation of their physical reality. Finally, he has concluded that, as long as appreciable atomic migration takes place, specific surface energies and surface tensions must be equivalent in solids as well as in liquids. Accordingly, the authors' eqs 2 and 3 can be written with equal accuracy in terms of interface tensions, simply by replacing each E_{ij} with its numerically and dimensionally equivalent interfacial tension γ_{ij}.

If the interfacial tensions (or specific energies) are independent of interfacial orientation, as is true in liquids, then the general equations that define the geometry at equilibrium of the common junction of three interfaces reduce to eq 1. However, neglect of the effect of boundary orientation is never completely justified theoretically[4] in dealing with crystalline solids; hence, use of eq 1 in such cases must always be considered as an approximation, though clearly a reasonable one for many purposes.[1, 2] At the same time, one should not be surprised that the assumption that interface tensions in solids are free from orientation

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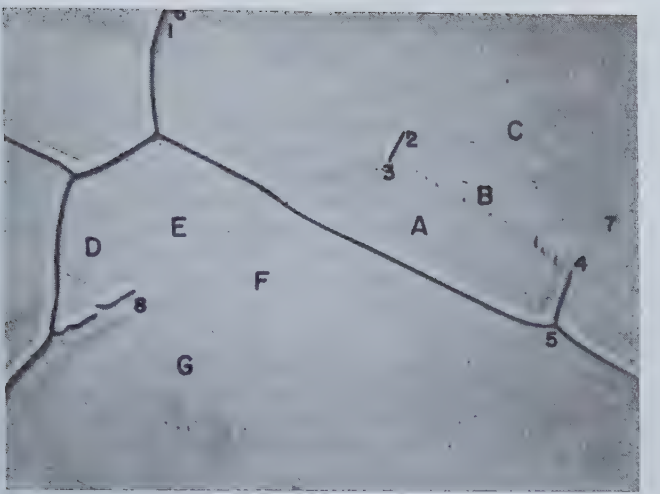

Fig. 14—Thermal grooves at the boundaries of twin related grains in high purity copper.

Grain pairs *AB*, *BC*, *DE*, *EF*, and *FG* are twin related. Thermal etch in hydrogen at 950°C for 1 week. X250.

dependence lacks generality; one should expect,[4] instead, that some interface tensions will be sensitive to interface orientation.

The authors have demonstrated convincingly that the interface between twin related crystals in body-centered silicon ferrite belongs to that class of interfaces whose orientation dependence cannot be ignored. Fig. 14 demonstrates qualitatively that the interface between twin-related crystals in the face-centered cubic system also falls into the same category. The micrograph shows high-purity copper that had been thermally etched in a hydrogen atmosphere at 950°C. The grooves at the grain interfaces are a surface tension effect[17] representing the equilibrium between the tensions of the copper (solid)—vapor interfaces and the copper (solid)—copper (solid) grain boundaries. The lattices of grains *A* and *B* are twin-related (as are also the grain pairs *BC, DE, EF* and *FG*). Shallow grooves, indicating relatively low tension in the grain boundary, are seen, e.g., in the boundary segments 1-2 and 6-7, where the interfaces correspond to the (111) planes that are common to the lattices of both adjacent grains. Deeper grooves, indicating higher tension, e.g., in the boundary segments 2-3 and 4-5, are found for other interface orientations between the same grains. This indication of greater tension in the segment 4-5 is further supported by the dihedral angles produced at the three-boundary junction 5, where the angles are all roughly equal, while the differently oriented twin boundary segment 1-2 has negligible effect at the triple-point 1.

The Herring equations, eq 2, cannot be completely general in defining the geometry at equilibrium of three-boundary junctions, for the triple-point displacements assumed for their derivation may not be attainable in certain cases, where one or more of the boundaries involved has a significant orientation dependence. For example, Nielsen,[18] Smith,[19] and Shockley and Read[4] have discussed the limitations when one of the boundaries is a twin interface, and the only possible junction displacements are either an extension or contraction of the twin interface.

Evidently, however, significant orientation dependence is not confined to the case of twin boundaries, for I have occasionally observed segmented boundaries, analogous to the boundary 1-5 in fig. 14 and therefore similarly indicating significant orientation dependence of the interface tension, in certain other instances that are now being studied in detail. It appears possible, for example, that the case can occur where two of the interfaces at a three-grain junction are highly orientation dependent. The junction numbered 8 in fig. 14, involving successively twinned grains, is certainly one such case, but microstructures suggesting greater generality for this case have also been observed. At such a junction no displacement of the triple point is possible and the only adjustment in junction geometry that can occur is a rotation of the orientation insensitive boundary. Radical rotations, however, may be limited by the constraints from neighboring junctions. Such possible constraints were not considered in the Herring derivation, and hence may further limit the generality of his equations.

In summary, therefore, it can be stated that, since interface tensions having significant orientation dependence must be treated by modified forms of the generalized equations, any attempt to relate various boundary energies by means of measurements of three-grain junction geometry can only be truly accurate if coupled with *a priori* knowledge of the orientation dependence of the interfaces involved.

C. G. Dunn, F. W. Daniels, and **M. J. Bolton** (authors' reply)—The authors wish to thank Professor Nielsen and Mr. Hess for their comments. Regarding surface tensions, it may appear from our preference of expressing equilibrium through the minimization of the total free energy of the grain boundaries, rather than through the equilibration of a system of forces, that we questioned the existence of surface tensions. This, however, is not the case. Our problem was one of procedure, because it did not seem unreasonable to question the identity of energy per unit area and surface tension for the case when energy varies with boundary orientation (in this case the surface tensions do not form a closed triangle of forces; additional forces at right angles to the boundaries enter the picture[8]). Consequently our decision was to use equations that expressed the minimization of total grain boundary energy.

In this connection it is interesting to note that Gurney[16] starts with energy concepts in proving that surface tension is a valid concept for the free surface of a solid and for proving specific surface energy equals the surface tension when there is sufficient atomic mobility at the surface to create an equilibrium density of atoms. At equilibrium temperatures the surface is considered to be a liquid layer. Applied to the present problem one would conclude that boundary and orientation effects would vanish and the equilibrium angles would be 120° at temperatures where boundaries become essentially liquid in nature. The present view regarding the nature of grain boundaries, however, is that they fulfill the transition lattice theory better than the liquid layer theory.[20]

Some of the limitations of eqs 2 and 3 mentioned by Mr. Hess were also discussed in the text, particularly with reference to specimen *G*.

Mr. Hess has shown some very interesting data for copper. Since these results also emphasize the importance of grain boundary orientation effects, his further work in this field will be followed with considerable interest.

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Titanium Binary Alloys

by C. M. Craighead, O. W. Simmons, and L. W. Eastwood

DISCUSSION, W. C. Ellis presiding

W. C. Ellis—Some of the micrographs show characteristic straight-line markings suggestive of Widmanstätten structure. Have the habit planes of these markings been identified?

Titanium has been reported in earlier publications to possess good corrosion resistance in many environments—particular mention has been made of salt water. In alloying to achieve higher physical properties are the corrosion properties adversely affected?

C. M. Craighead, O. W. Simmons, and **L. W. Eastwood** (authors' reply)—Alloys normally all alpha or largely alpha at room temperature will show a Widmanstätten structure when they have been cooled from the beta field. This is, of course, entirely within expectations. We have not established the planes upon which the precipitation takes place.

No data on the resistance to corrosion of the alloys are available, but this information is being obtained.

H. E. Stauss—The authors have melted a very reactive metal containing a large amount of oxygen (0.14 pct) and have relied upon a neutral atmosphere to remove the oxygen. Can the effective oxygen content be reduced further by the use of some addition to fix or stabilize the oxygen?

C. M. Craighead, O. W. Simmons, and **L. W. Eastwood**—We know of no method of removing oxygen from titanium without reprocessing it. Because of the strong affinity for oxygen, most reducing agents are probably not effective. We did not use an inert atmosphere to remove oxygen, as implied by Mr. Stauss. Instead, we use an inert atmosphere during melting to prevent contamination with oxygen as well as other impurities.

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Some Observations on the Recovery of Cold Worked Aluminum

by T. V. Cherian, P. Pietrokowsky, and J. E. Dorn

DISCUSSION, W. L. Fink presiding

H. Schwartzbart and **W. F. Brown, Jr.**—The authors have divided the effects of recovery on the true stress-true strain curve into two types; metarecovery, which effects only the first part of the curve or the yield strength, and orthorecovery, which effects the flow stress at any strain. Both of these are said to be true recovery effects, involve no recrystallization, and are explained by the removal of two different types of imperfections caused by work hardening.

However, there seems to be some question as to whether the data are sufficiently conclusive to exclude, as an explanation of the authors' results, a mechanism based on the relief of residual stresses between the grains or slip bands and recrystallization. It appears that metarecovery could be interpreted in the same fashion as a customary interpretation of the Bauschinger effect. The balanced system of internal stresses which exists between grains in a strained specimen due to varying orientation and, hence, yield strengths, of the different grains is responsible for a reduced yield strength in compression following pre-tension, and, similarly, for an elevated yield strength in tension following pre-tension. If the specimen is now heated so that the internal stresses are relieved by creep, then the yield strength in tension following tension will have been reduced and in compression following tension will have been raised.

There seems to be a very strong case for the lack of recrystallization in the aluminum investigated by the authors, if one defines recrystallization as the presence of visually detectable new grains or accepts the X-ray evidence as conclusive. One must remember, however, that the appearance of spots on the back-reflection X-ray patterns cannot be taken as the time when recrystallization first started. The areas of recrystallized strain-free material must first have grown to a size large enough to give distinct spots on the patterns and this may take some time. Averbach[17] in an investigation of brass has shown that recrystallization can be detected by extinction measurements at temperatures lower than those based on hardness or X-ray line width determinations. It can be seen from fig. 10 that the rate of recrystallization is extremely low over a considerable time period at the onset of the process. Observations on the rate at which small amounts of recrystallization effect the flow stress would have given further insight as to whether undetectably small amounts of recrystallization might have been responsible for orthorecovery. Also, the question arises as to whether the effects observed in fig. 6 for various times and temperatures could not have been obtained if the time at 212°F were sufficiently long. In addition, the argument that the curve in fig. 10 is not sigmoidal seems weak in view of the scattering of the points. It is conceivable that an accurate determination of the curve for the first 100 hr would exhibit a relationship other than the one drawn.

There is one point we would like to raise about the condition of the starting material. The authors annealed their material at 750°F for 15 min to remove the effects of any previous work hardening or machining strains. Reference to the work by Anderson and Mehl shows that this treatment may not have completely recrystallized the aluminum, so that the starting material may have had some strained areas. Higher temperatures or longer times may have been required to remove the effects of any small strains.

We would like to mention some results of tests being conducted at the Lewis laboratory of the National Advisory Committee for Aeronautics in an investigation of the Bauschinger effect in relation to fatigue. Tests were performed on annealed electrolytic copper and several annealed brasses. Specimens were prestrained 1 pct in tension and then tested in compression or tension with and without intermediate stress-relieving annealing treatments at 500°F for various times. Specimens heated at 500°F for 10½ hr showed an elevation of the flow curve in compression and an approximately equal lowering of the flow curve in tension when compared with the curves for the unheat treated specimens. After approximately 0.8 pct strain, all flow stresses coincided and were equal to the flow stress of the virgin material at this strain. This behavior is consistent with the metarecovery observed for aluminum by the authors and for which a residual stress model can be used. On the other hand, increasing the recovery time to 15½ hr resulted in a flow stress in subsequent tension which was below that for the virgin material at all strains, i.e., orthorecovery was obtained. We would like to raise the point that this seems to be inconsistent with a two-mechanism process of recovery. It would seem to us that once only metarecovery was obtained, further time at the temperature in question should not produce orthorecovery, since this process requires a higher activation energy which could be reached only by increasing the temperature.

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[17] B. L. Averbach: Recovery and Recrystallization in Brass. *Trans.* AIME, 185, 491-494; *Journal of Metals* (Aug. 1949) TP 2636E.

H. SCHWARTZBART and W. F. BROWN, JR., National Advisory Committee for Aeronautics, Cleveland, Ohio.

The behavior of brass is entirely different. Recovery treatments are possible which reduce greatly the magnitude of the Bauschinger effect (i.e., raise the 0.1 pct yield strength in subsequent compression approximately 90 pct, but do not change the 0.1 pct yield strength in subsequent tension more than 5 pct). It would seem that strain aging is acting as a complicating factor in the behavior of the brass.

Summing up, it would seem to require more proof to show that different recovery mechanisms are responsible for the observed phenomena and that it is not actually merely relief of residual stresses and recrystallization. According to our understanding, it would be necessary to show conclusively that at no temperature would it be possible to get metarecovery after which orthorecovery would begin at longer times.

T. V. Cherian, P. Pietrokowsky, and **J. E. Dorn** (authors' reply)—The authors wish to thank Messrs. Schwartzbart and Brown for their interesting and stimulating discussion. The anneal preliminary to strain-hardening the tensile specimens was introduced in order to place the specimens in some standard state. The rather good agreement between the stress-strain curves of the various specimens preliminary to the recovery treatment strongly suggested that this objective had been achieved. Undoubtedly the recovery of the Bauschinger effect does attend what we have termed "metarecovery." This effect can be visualized, in part, as a relief of microstresses on slip bands due to the interaction of various grains and their substructures, resulting from the accumulation of dislocations near the boundaries of the substructures and grains. It is quite possible that the migration of dislocations under the action of the residual microstresses attends the annealing. Inasmuch as no study of the Bauschinger effect was made in the present investigation, it was considered inadvisable to ascribe what was termed "metarecovery" as solely a recovery of the Bauschinger effect.

Messrs. Schwartzbart and Brown suggested that what we have termed "orthorecovery" might actually be recrystallization. This interpretation of "orthorecovery" appears to be at variance with the commonly accepted process of recrystallization, namely nucleation and growth. Such processes always yield sigmoidal types of fraction transformed vs. time curves due to the fact that before growth occurs stable nuclei must form. During the preliminary stages of recrystallization, the number of nuclei are so small or their surface area is so small that the rate of recrystallization is low. But, as the pre-existing nuclei grow and as more nuclei form, the rate of growth increases and reaches a maximum value. Thereafter the rate of recrystallization decreases because of the impingement of growing grains upon each other. Only when the rate of nucleation is infinite can the process of recrystallization start with a maximum rate. In contrast to the above picture for recrystallization, "orthorecovery" has its greatest rate at the start of the annealing treatment. This is shown more accurately in a recent paper.[18] Since the greatest rate of "orthorecovery" was observed at low temperatures where the nucleation rate is known to be low, it follows that "orthorecovery" is distinctly different from the process of recrystallization as pictured above.

The statement by Messrs. Schwartzbart and Brown, that ". . . once only metarecovery was obtained, further time at the temperature in question should not produce orthorecovery, since this process requires a higher activation energy which could be reached only by increasing the temperature," is unacceptable to the authors. According to the general tenets of reaction rate theory both reactions can occur simultaneously, but that reaction which has the higher activation energy occurs more slowly. At low temperatures and short times the process having the lower activation energy predominates. At higher temperatures the process of lower activation energy occurs very rapidly and is then followed by the process of higher activation energy. In the present cases of "meta" and "orthorecovery," it appears as if the process of "orthorecovery" occurs after the "metarecovered" state is achieved.

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[18] T. E. Tietz, R. A. Anderson and J. E. Dorn: Effect of Prestraining Temperatures on the Recovery of Cold Worked Aluminum. *Trans.* AIME, 185, 921; *Journal of Metals* (Dec. 1949) TP 2716E.

Effect of Prestraining Temperatures on the Recovery of Cold Worked Aluminum

by T. E. Tietz, R. A. Anderson, and J. E. Dorn.

DISCUSSION, W. L. Fink presiding

D. H. Woodard—Work completed some time ago on the behavior of the flow curves of Monel suggests that more might be involved in the lowering of the flow curve than the phenomenon of recovery. When flow curves are obtained, at room temperature, on 0.505-in. specimens, following the type of deformation at elevated temperature known as creep, results similar to those shown in fig. 8 are obtained. The top curve is approximately that of annealed Monel carried to fracture at room temperature. The other curves were similar to those obtained at room temperature on specimens that had been (1) prestrained 0.1 pct at room temperature, (2) brought to 900°F in a creep furnace, (3) loaded similarly as creep specimens, (4) allowed to deform in creep to the beginning, the middle, and the end of the second stage of creep respectively. As these specimens were allowed to stand, without load, for four days, it was felt that macrorecovery had been completed.

To investigate the microstructural differences in the four specimens, the sectioned surfaces were made optically active under polarized light. Fig. 9 shows the effect of increasing plastic deformation on the microstructure of the annealed specimen. Here, within any one grain, a difference in intensity represents a difference in orientation. It is evident that increasing plastic deformation results in increasing distortion of the grains. Fig. 10 shows an area within ⅛ in. of fracture of a specimen fractured at room temperature after being carried to the end of the second stage of creep. Not only are the grains not as severely elongated

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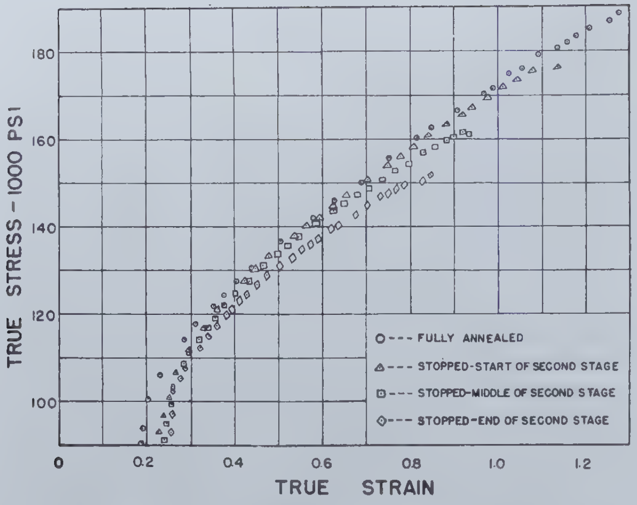

Fig. 8—Creep specimens given 0.1 pct strain at 76°F before being loaded at 900°F.

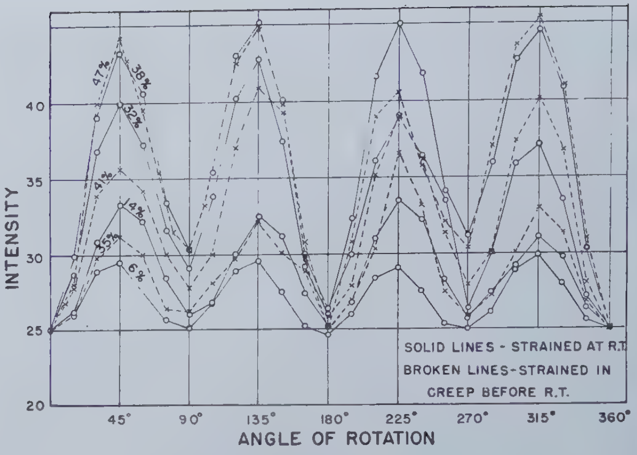

Fig. 11—Effect of prior creep on the development of a fiber texture during room temperature deformation.

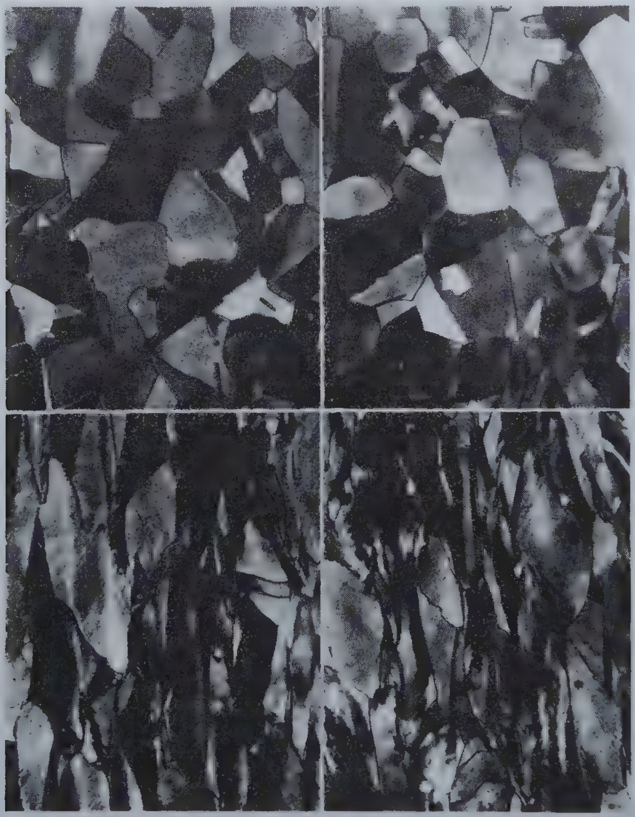

Fig. 9—Variations in intensity patterns within individual grains in Monel metal after plastic deformation in tension. The axis of tension is in the vertical direction for all specimens. X750.

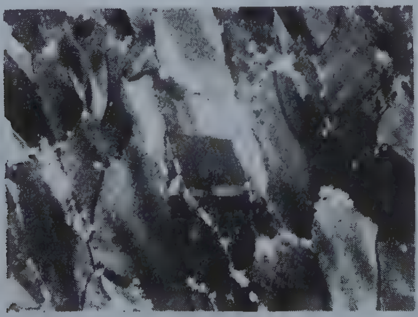

Fig. 10—Specimen fractured at room temperature following end second stage of creep. X750.

but the distortion within any one grain is less. This suggested that the amount of preferred orientation developed was less after creep than after the same extension at room temperature.

If one measures the integrated intensities from several hundred grains as the plane of polarization is rotated, solid curves, such as those shown in fig. 11, result. As increasing plastic deformation results in an increase in the sharpness of the peaks, it is assumed that this is a quantitative measure of the development of preferred orientation. When this technique (which is apparently more sensitive than X-rays) is applied to specimens that have been strained equal amounts in creep before pulling at room temperature, dashed curves of the type shown result. It becomes apparent then that the more a specimen deforms in creep, the easier it becomes for it to deform at a lower temperature without developing a preferred orientation texture.

The authors conclude, from the varying slopes of fig. 1, that the rate of strain hardening is different at the two temperatures. As the rate of strain hardening is less after creep, it is evident that the rate of change in the amount of distortion in the grains determines the rate of strain hardening. Further evidence of this sort has been obtained at the National Bureau of Standards and is, I hope, to be reported shortly.

T. E. Tietz, R. A. Anderson, and **J. E. Dorn** (authors' reply)—We wish to thank Mr. Woodard for his interesting contribution. The last sentence of the first paragraph of Mr. Woodard's discussion is not clear to the authors inasmuch as it is not stated whether the temperature at which the "specimens were allowed to stand, without load" was 900°F or room temperature. In addition the data recorded in the second paragraph of Mr. Woodard's discussion are not satisfactorily identified insofar as it is not certain whether the total strain during creep at 900°F and subsequent straining at room temperature was greater, less than, or equal to the straining at room temperature in the specimen used for comparison. In the fourth paragraph of his discussion Mr. Woodard states that "The authors conclude, from the varying slopes of their fig. 1, that the rate of strain hardening is different at the two temperatures." But curves *C* to *D* and *F* to *H* of our data were obtained at the same temperature with the two designated alternate prestrain histories. The two dissimilar slopes for curves *C* to *D* and *F* to *H* show that the rate of strain hardening does depend on the prestrain history. The difference in the degree of preferred orientation between states *F* and *C* was less than that which could be detected by the usual X-ray procedures. The authors hope that the technique developed by Mr. Woodard will be adapted to clarify how much of the failure of the mechanical equation of state might be due to preferred grain orientation.

The Properties of Sand Cast Magnesium-Rare Earth Alloys

by T. E. Leontis

DISCUSSION, H. Y. Hunsicker presiding

H. E. Stauss—This research shows that the best high-temperature properties were secured by use of an element that went into solid solution and not by use of the elements that produced complex structures. Would it not be true, if a complex structure could be produced together with the strengthening effect of solution, that further improvement in high-temperature properties could be secured?

T. E. Leontis (author's reply)—It is true that the highest elevated-temperature properties were obtained with the rare earth metal that exhibits the greatest solid solubility in magnesium. But the improvement in these properties is not limited to the compositional range of solid solubility; all the property vs. composition curves presented in the paper indicate that strength and creep resistance continue to increase with composition in alloys well beyond the solid solubility limit.

It can be shown by detailed evaluation of the data that the presence of lanthanum in these alloys contributes nothing to the strength properties. For example, Mg + 6 pct Ce-free Mischmetal contains 3.2 pct didymium and 3.1 pct lanthanum. The creep limit based on 0.1 pct creep extension of this alloy is 13,500 psi at 400°F and that of an alloy containing 3.2 pct didymium only is also 13,500 psi (see fig. 18). Similar comparisons can be made with other properties and at various composition levels. In all cases it will be found that the presence of lanthanum in Mg-Ce-free Mischmetal alloys effects no further enhancement in the properties over those of the corresponding Mg-didymium alloy. Inasmuch as lanthanum is the least soluble rare-earth metal in magnesium, the above observations lead to the conclusion that for a further improvement in high-temperature properties, a metal that has an appreciable solubility in magnesium must be combined with Mg-didymium alloys.

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Some Effects of Phosphorus and Nitrogen on the Properties of Low Carbon Steel

by G. H. Enzian

DISCUSSION, J. J. Heger presiding

A. B. Wilder—The data presented by Mr. Enzian are of fundamental importance to the manufacturers of low-carbon steel. The type of deoxidation, particularly with respect to the use of aluminum, as the author has indicated, is related to the work brittleness test results. The presence of aluminum is apparently related to nitrogen "fixation." Material used in the investigation was normalized at 1650° to 1675°F. It has been our experience that normalizing influences results obtained in the work brittleness test. Hot-rolled carbon steel pipe is generally used in the as-rolled condition and comments regarding the work brittleness test results of this type of material would be of interest.

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Intergranular Parting of Brass during Anneals

by F. H. Wilson and E. W. Palmer

DISCUSSION, G. Edmunds presiding

W. C. Ellis—The intergranular fracture observed by these authors in brass seems to be characteristic of metals when tested under similar conditions. It has been observed by us in room temperature tests on lead alloys subjected to constant stress when the stress has been low enough to afford a small strain rate. If, however, the test be carried out at a high stress and therefore at a large strain rate, a characteristic, tapered, transcrystalline fracture is obtained. The same change of fracture has been observed by others with decrease of strain rate and increase of temperature for other metals—for example aluminum—and may be presumed, as the authors point out, to be general for metals.

These findings suggest a plastic flow mechanism under conditions of small strain rate and high corresponding temperature differing from classical block slip. The required conditions point to a process fundamentally diffusive in nature—a less organized process than block slip. Nabarro[18] has shown that plastic flow can occur by stress induced diffusion of vacant sites—a process of self-diffusion. Movements of a pseudo-viscous nature at grain boundaries are suggested in the work of Kê.[15] Deformation near to a grain boundary by other than a slip mechanism appears necessary to Boas and Hargreaves.[19] Wood and Rachinger[20] report a cellular structure in slowly deformed aluminum—the cell size is larger, the higher the temperature and the slower the strain rate. Presumably in the latter case diffusive movements occurred in the cell boundaries. In any case the nonslip mechanism seems somewhat obscure and further work is indicated. Such studies will undoubtedly clarify the nature and behavior of lattice imperfections—the very core of the strength and plastic properties of metals.

F. H. Wilson and **E. W. Palmer** (authors' reply)—It is certain that the metallic behavior which has been termed "creep" includes many interdependent phenomena of which a nonslip type of plastic flow may well be one. The reports to which Mr. Ellis refers are illustrative of the many different observations that must be correlated for a complete understanding of creep. The list could be extended considerably. For example, we ourselves have been impressed by the sensitivity of creep phenomena to the presence of minor impurities and feel that this aspect of the problem warrants more thorough study than it has yet received.

W. C. ELLIS, Bell Telephone Labs., New York, N. Y.

References

[18] F. R. N. Nabarro: Report of Bristol Conference on Strength of Solids. P. 75, (1948) London.

[19] Boas and Hargreaves: *Proceedings* Royal Society. (1948) **193**, 89.

[20] Wood and Rachinger: *Journal* Institute of Metals. (1949) **17**, 237.

Effect of Solute Elements on the Tensile Deformation of Copper

by R. S. French and W. R. Hibbard, Jr.

DISCUSSION, G. Edmunds presiding

G. W. Geil—The authors have presented data showing the effect of the solute elements on the true stress and strain values for various copper alloys. Linear logarithmic true stress-strain curves are shown and the slopes of the straight lines beyond the yield strength region were considered as the work-hardening coefficients (the exponent m of the parabolic true stress-strain relation $S = ke^m$, eq 1 in the paper).

Unpublished test data that have been obtained recently at the National Bureau of Standards with OFHC copper and other nonferrous and ferrous metals and alloys tested in tension at room and subzero temperatures, however, do not conform to a linear relationship when the true stress-strain values are plotted on logarithmic coordinates. These tests were made with standard cylindrical tensile specimens, and numerous simultaneous load and diameter measurements were taken during the entire deformation of the specimen up to the fracture. The slope of the logarithmic true stress-strain curves at the maximum load were equal to the strains at the maximum load, as expected. However, the portion of the curves between the yield strength region and the maximum load were not linear, and the true stress-strain values deviated greatly from the straight lines drawn through the maximum load points with the slopes equal to the strains at the maximum load. The results lead me to question the shape of the curves for strains above 0.01 as presented by the authors. Perhaps, due to the method of testing, either the dimensional measurements of the specimen after the release of the load may have been affected by some recovery in the metal, or the determination of the effective strain for rectangular specimens according to eq 2 of the authors' paper may have given questionable results. In view of the results we have obtained, I believe that true stress-strain data for copper and many other metals do not necessarily confirm a parabolic true stress-strain relation of the type $S = ke^m$, and that the slope of the straight lines obtained by the authors may not represent accurately a true strain-hardening coefficient.

C. S. Barrett—These results, like those of Brick, Martin, and Angier, show the unusual position of Cu-Si alloys among the copper-rich solid solutions and suggest that stacking faults may be involved. If this is the case, one would expect alloys containing 9 to 12 atomic pct silicon to be even more anomalous than the ones studied here, for the tendency to faulting increases rapidly in this range of compositions.[8]

G. W. GEIL, National Bureau of Standards, Washington, D. C.; C. S. BARRETT, University of Chicago, Chicago, Ill.

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[8] C. S. Barrett: *Trans.* AIME 188, 123; *Journal of Metals* (Jan. 1950) TP 2754E.

Electrical Resistivity and Thermoelectric Power of Antimony-Selenium Alloys

by B. D. Cullity, M. Telkes, and J. T. Norton

DISCUSSION, B. W. Gonser presiding

M. Balicki—As one who some years ago spent much time searching for an alloy with high thermoelectric power that would be suitable for heat energy-electric energy converter based on the principle of a thermoelectric pile, I would like to make a few comments touching upon that aspect of this excellent paper. The specifications which one of the authors has formulated so aptly do not appear to me as complete, and I would like to add to them the following two demands: (1) Melting point not less than 500°C and (2) elongation on 2 in. at least 5 pct. Condition 1 would insure good thermodynamic efficiency of the pile by permitting a reasonably high temperature of the hot junction and at the same time making it suitable for such application as salvage of vast amounts of energy which is lost in the form of sensible heat of waste gas leaving industrial and other furnaces. Condition 2 is also a very important one; particularly, because of the fact that all elements and alloys which exhibit attractive thermoelectric properties seem to be as a rule very brittle. The design, erection, and maintenance of a pile incorporating a brittle material in one of the most crucial parts of the converter would be a very difficult and costly affair indeed.

To illustrate this point I may mention great difficulties I encountered when trying to make thermocouples of silicon. Casting of ¼-in. rods in iron or graphite mould yielded only broken pieces which had to be welded into a bar. Such a bar had to be handled very carefully during the determinations. Raising the molten silicon by vacuum into a silica tube and solidifying it there solved the problem of stability as well as that of electrical insulation of a bar. On tests this bar (98.5 pct Si) showed $dE/dT = -275.5$ microvolts per degree C vs. copper. Thermocouples made of this grade of silicon and pure nickel developed 0.39 v when temperature of the hot junction was approximately 1000°C. The possibility Dr. Gonser has mentioned of trying to impart to metals good thermoelectric properties by alloying them with silicon, has been considered. The preliminary survey which I have made was, however, disappointing. Perhaps, it will be advisable to record the results obtained (table VI), as this might save repetition of search in fields already covered.

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Table VI. Thermoelectric Power (Relative to Copper) of Some Binary and Ternary Alloys of Plastic Metals with Silicon in As-Cast Condition

Crucible Charge, Composition, Pct	dE/dT (Relative to Copper), Microvolts per Degree	Crucible Charge, Composition, Pct	dE/dT (Relative to Copper), Microvolts per Degree
Fe-100; Si-0	+ 7.54	Ni-100; Si-0	—22.9
Fe-98; Si-2	— 9.22	Ni-98; Si-2	—18.9
Fe-96; Si-4	— 8.60	Ni-94; Si-6	—15.0
Fe-94; Si-6	—11.08	Ni-90; Si-10	— 8.68
Fe-92; Si-8	—10.27	Ni-80; Si-20*	—14.6
Fe-90; Si-10*	— 6.46	Co-54.5; Si-45.5*	— 2.44
Fe-85; Si-15*	+ 0.49	Sb-100; Si-0*	+37.1
Fe-79; Si-21*	+ 4.99	Sb-?; Si-?* (evaporation)	+18.3
Cu-100; Si-0	0.00	Mn-98; Si-2*	— 4.01
Cu-98;Si-2	— 1.69	Mn-96; Si-4*	— 2.91
Cu-96; Si-4	— 1.25	Mn-88; Si-12*	+11.02
Cu-94; Si-6	— 0.82	Cu-87.3; Si-6.5; Mn-6.4	— 1.96
Cu-94; Si-6 quenched	— 0.91	Cu-83.7; Si-7.6; Co-9.4	— 3.04
Cu-92; Si-8	— 6.29	Cu-77.8; Si-4.2; Ni-18.0	— 4.41
Cu-90; Si-10	— 3.72	Cu-42.9; Si-28.4; Ni-28.7	— 1.31
Ag-90; Si-10	— 1.95	Cu-39.0; Ni-59.0; Co-2.0	—34.3
Ag-60; Si-40	— 0.85	Cu-58.0; Ni-38.0; Co-4.0	—28.3
		Cu-54.0; Ni-36.0; Mn-10.0	—18.0

* Alloy very brittle.

A system related to the one the authors have investigated, namely Sb-Cd, has also been surveyed. As in the author's case, the antimony side of the system, from the thermoelectric properties point of view, is uninteresting up to the composition approximately 50 pct of cadmium. Compositions in the vicinity of the composition corresponding to Cd-Sb compound exhibit high thermoelectric power, that seemingly depends upon the conditions of cooling, which in turn influence the formation of Cd_3Sb_2. Here again all the interesting alloys (with dE/dT greater than 200 microvolts per degree) were exceedingly brittle and had to be vacuum-cast into pyrex tubes to permit a safe handling. The data obtained during this exploratory work are quoted in table VII.

B. D. Cullity, M. Telkes, and **J. T. Norton** (authors' reply)—We are very glad to receive Dr. Balicki's discussion, particularly as it includes some original data on the thermoelectric power of alloys. Regarding the criteria to be used in selecting an alloy for use in a thermoelectric generator, we feel that those mentioned in the paper are of primary importance inasmuch as the properties involved determine the thermoelectric efficiency. Besides having the proper electrical and thermal properties, an alloy should have, as Dr. Balicki states, a reasonably high melting point and good ductility. Still other desiderata that might be added are stability at the operating temperature and low cost.

Table VII. Thermoelectric Power of Certain Sb-Cd Alloys in As-Cast Condition

Antimony in Crucible Charge, Pct	dE/dT (Relative to Copper), Microvolts per Degree
100	+ 37.10
40	+ 5.53
45	+ 6.10
46.6	+ 4.90
48.4	+ 9.50
50.0	+ 21.40
51.7	+145.00
53.4	+185.0
55.0	+155.0
50-55*	+248.0
50-55*	+257.0
50-55*	+520.0
55.7	+129.0

* Compositions uncertain due to losses on re-melting, different solidification rates employed.

The thermoelectric power data presented by Dr. Balicki are indeed welcome. It would be interesting to know the electrical resistivity of the silicon used and of the cadmium-antimony alloys, since both materials possess thermoelectric powers in the right range for use in generators.

Effects of Three Interstitial Solutes (Nitrogen, Oxygen, and Carbon) on the Mechanical Properties of High-purity, Alpha Titanium

by W. L. Finlay and J. A. Snyder

DISCUSSION, B. W. Gonser presiding

G. Edmunds—Solid solubility is considered to be of either the interstitial or the substitutional type. Is it possible, in a binary alloy as the simplest case, that some of the solute atoms are present in the normal lattice sites (substitutionally or filling lattice vacancies) while simultaneously others are in interstitial positions? One might even ask whether a distribution of the two types may be the normal situation.

H. M. Meyer—Metastable states of interstitial atoms occupying vacant lattice sites possibly occur as well as of substitutional atoms squeezed in between regular matrix positions. However (as we know since Hume-Rothery), the solute atoms choose between the two kinds of solutions; consequently, every solute will be unequivocally either substitutional or interstitial in the equilibrium state of the solid solution.

M. Balicki—In view of the fact that the authors apparently correlate the analysis of the alloys at the *ingot stage* with the properties exhibited at the *testing stage,* I would like to ask whether this is a fully justifiable procedure. In other words, how good are their determinations of solute concentration for correlating them with the mechanical properties. The answer to this question may explain some of the divergencies. Assuming good enough homogenization of the samples and exact determination of mechanical properties the position of the plotted experimental points will depend solely upon the accuracy of composition determination. If this is not accurate, say due to loss or pickup of elements during processing from the ingot to the testing stage, or due to a systematic error in the method employed for obtaining solute concentration data, the points will deviate from their true position and may align themselves along a different curve than the one expected.

H. V. Kinsey—We have been studying the creep-rupture properties of titanium-base alloys at 1000°F. In the course of this work, anomalies in behavior of the alloys that would suggest that the material under test was becoming stronger as the test progressed have been observed. If this was so, the most likely explanation that we could think of was that the test bars were absorbing oxygen and nitrogen from the air during the test and were thereby becoming strengthened.

In an attempt to determine the strengthening effect of absorbed oxygen and nitrogen the following experiment was conducted.

A length of cold-rolled titanium was supplied by the E. I. du Pont Co. Two test bars, having a ¼ in. diam gauge length, were prepared from this material. One bar was tested in the as-received condition. The second bar was heated in air at 1550°F for 100 hr and subsequently air cooled prior to testing. A testing temperature of 1000°F was employed. The results of these tests are tabulated in table II.

Table II. Results of Tests on Cold-Rolled Titanium

Condition of Test Bar Material	Hr at 7000 psi	Hr at 8550 psi	Hr to Fracture	Hr to 4 Pct Creep Stress	Total Elongation, Pct	Total Reduction in Area, Pct
As-received	235		235	95	26	84.3
Heat-treated	667	187	854	650	23	71.8

In the author's opinion, is it reasonable to assume that the bar that was exposed to air at 1550°F for 100 hr was stronger because it absorbed oxygen and nitrogen from the air during this heat treatment?

W. L. Finlay (authors' reply)—Direct experimental evidence for or against Mr. Edmunds' interesting suggestion will probably never be available. It seems possible, however, that mixed interstitial-substitutional solid solution might well occur with interstitial elements. The less likely possibility of interstitial solution of a normally substitutional element like copper in aluminum was recently discussed at length by the

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Table III. Parameter-Composition Data

	Wt, Pct	a_0	c_0	c_a	Vickers Hardness No.
Carbon	0.0	2.9504	4.6834	1.5873	103
	0.1	2.9517	4.6883	1.5884	141
	0.2	2.9530	4.6932	1.5894	153
Oxygen	0.0	2.9504	4.6834	1.5873	103
	0.055	2.9504	4.6843	1.5876	150
	0.105	2.9504	4.6852	1.5879	175
	0.19	2.9504	4.6868	1.5884	207
Nitrogen	0.0	2.9504	4.6834	1.5873	103
	0.05	2.9505	4.6845	1.5876	165
	0.10	2.9506	4.6856	1.5880	195
	0.15	2.9507	4.6867	1.5883	215

British Institute of Metals.[16] The negative view prevailed, but the disposition of the matter was not completely conclusive.

The important point raised by Dr. Balicki is discussed in the "Analysis of Chemical Composition" section of the paper, pages 281-282.

Mr. Kinsey's assumption that 100-hr air exposure at 1550°F of a ¼ in. diam test bar would strengthen it by the absorption of oxygen and nitrogen is indeed reasonable.

Parameter-composition data is given in table III.

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[16] F. Rohner: Discussion on A Theory of the Age-Hardening of Aluminum-Copper Alloys, Based on Vacant Lattice Sites. *Journal Institute of Metals.* (1947) 73, 768-785.

A Preliminary Investigation of the Zirconium-Beryllium System by Powder Metallurgy Methods

by H. H. Hausner and H. S. Kalish

DISCUSSION, S. Tour presiding

M. Hansen—This paper certainly is an interesting study. Although I have not had too much experience in the powder metallurgical methods of studying phase equilibria, I would like to say the following concerning the interpretations of the results obtained:

1. The existence of a zirconium-rich eutectic having a melting point close to 950°C and containing approximately 5 pct beryllium is well established.

2. Undoubtedly sintering of the original compacts (i.e., without repressing and resintering at 1350°C) resulted in a condition being far from equilibrium, even in the low-melting point zircon-rich region where undissolved zirconium particles have been observed. This means that only partial reaction between the component powders has taken place.

3. In preparing and handling powder mixtures for pressing and sintering, we have found that with powders differing considerably in density, and also in particle size, separation in layers of different composition may occur. This means that a concentration gradient would exist within such samples. This phenomenon may, at least to some extent, account for the difference in microstructure of the top and bottom regions of some of the sintered samples. If this is the case, density figures for some of the nominal compositions would not represent actual densities of those mixtures.

4. Fig. 1 shows that the low densities of mixtures with 40 and 60 pct beryllium sintered at 1350°C are changed to much higher densities if the products sintered at 1100°C are repressed and resintered at 1350°C, whereby an approach toward equilibrium takes place. This would mean that the low density and growth in volume is due to nonequilibrium conditions. If this is true, would it be justified, then, to conclude that "the remarkable growth of the alloys in the vicinity of 40 to 60 pct Be indicates the formation of a high-melting point phase, probably accompanied by a considerable change in volume due to a large alteration of the crystal structure from that of the original compounds"? If some compound formation has taken place already during the first sintering at 950° to 1350°C, more compound would be formed by repressing and resintering of the 1100° samples. This treatment, however, results in higher, rather than lower, densities. In general, the density-composition curve of alloy systems containing one or more intermediate phases is characterized by a more or less defined contraction (decrease in specific volume, increase in density) over the "theoretical" density. Does not discrepancy exist between the two statements that "growth of the alloy indicates the formation of a high-melting phase . . ." and "even at 1350°C, no indications of sintering have been observed"?

5. I am not sure that the explanation given for the fact that fig. 4 did not reveal as much eutectic as the top portions of the mixture with 2 pct Be, is correct. The density of the melt containing only 5 pct Be or even perhaps less, is not too much different from that of the nominal composition. The reason might be also that there was already some separation of the components in the pressed compact.

6. I do not understand why the microstructure of the bottom regions of the compact with 5 pct Be (fig. 6) is so different from that of the top regions (fig. 5). The compact was melted on sintering at 1100°C. Its composition lies close to the eutectic point. There should be at least some lamellar structure in the bottom regions too; otherwise, the composition of top and bottom must have been very different after sintering, because the eutectic is said to extend as far as the composition $ZrBe_2$. In case the white and gray areas of fig. 6 are both gamma, and the black areas undissolved zirconium, this composition would be close to the phase coexisting with zirconium, that is, $ZrBe_2$, according to the hypothetical diagram, or a compound richer in zirconium.

7. Figs. 9 and 10 are not mentioned in the text.

8. The great difference in microstructure of the composition 20 pct Be of figs. 8 and 14 on one side and fig. 15 on the other side proves that sintering at 950° and 1100°C results only in partial reaction of the powers.

9. The mixture with 60 pct Be (fig. 19) seems to consist of two phases, rather than one phase, one interspersed in a matrix of another.

10. The statement that the eta phase "may be an intermetallic compound or the product of a peritectic or monotectic reaction" seems to be misleading, because the product of a peritectic or monotectic reaction in this region of the system must be an intermetallic compound.

11. If there is some solid solubility of Be in alpha and beta-Zr, it would be expected to be higher in beta-Zr (b.c.c.) than in alpha-Zr (h.c.p.). The temperature of the polymorphic transformation of zirconium then would be lowered, rather than increased. In accordance with this, Battelle has found that the transformation point of titanium is decreased by beryllium.

12. In case the phases present in alloys with 80, 90, and 95 pct Be are identical (which appears to be correct), it is striking that the relative amounts of both phases (eta and beryllium) are not too different within this wide range of composition. With 60 to 65 pct Be

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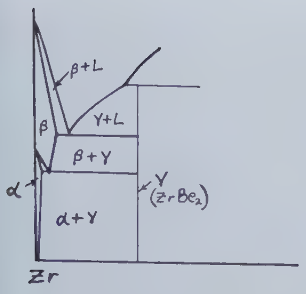

Fig. 25—Portion of Zr-Be diagram.

for the eta phase, the relative amounts of the eta phase in these alloys should be, roughly, 50, 30, and 15 pct, respectively. Using figs. 20 to 23 to determine the compound existing with beryllium by means of the lever rule gives inconclusive results; the composition of the eta phase, then, may vary between less than 60 and more than 80 wt pct Be.

13. As far as the proposed provisional phase diagram is concerned, it appears particularly interesting in addition to the beryllium-rich compound $ZrBe_2$ (66.7 atomic pct Be), there are three other intermediate phases richer in beryllium, of which the delta phase is shown to have a composition corresponding to the formula $ZrBe_4$ (80 atomic pct Be). The lattice structures of the other two phases, epsilon and eta, would be based on rather unusual compositions, i.e., between about 86 and 95 pct Be.

14. I was very interested in the method used to transform highly ductile zirconium into fine powder by converting it into hydride, etc.

H. S. Kalish (authors' reply)—I wish to thank Dr. Hansen for his careful examination of this paper and the valuable discussion he has afforded us. I shall attempt to answer each point in order.

1. The existence of a zirconium-rich eutectic was known to us by hearsay, but we could not find any published record of this work. If this information is in the literature, we should appreciate knowing the source.

2. While equilibrium may not have been attained throughout the samples in all cases the structures were very close to equilibrium. Beryllium apparently diffuses rapidly in zirconium so that the powder metallurgy approach wherein melting need not occur is favorable. This fact is clarified in table II where X-ray data are shown. Even sintering for 2 hr at 1100°C resulted in a structure free from zirconium when 80 pct Zr, or less, was present. At higher zirconium compositions we would expect the alpha phase of zirconium to be present as it is. Sintering at higher temperatures and for longer times seemed to have little effect on equilibrium, showing that a structure close to equilibrium had been attained. The reaction then was nearly complete, but, when the concentration gradient becomes small, final equilibrium cannot be attained in any practical length of time. Such small deviation from equilibrium, however, would not cause any gross movements in the preliminary phase diagram.

3. The powders were blended and pressed in a way that was found to give a good mixture. Furthermore the samples were relatively thin. Only where some melting occurred was a difference in microstructure apparent from top to bottom. In no case do we intend to imply that the density figures are those of the actual equilibrium composition. Frequently the sintered compact was extremely porous and the densities shown in table I and fig. 1 are actual gross density of the sintered compact. The upper solid line in fig. 1 represents the theoretical density based on a mixture of the two metals.

4. It has been frequently shown that heating a mixture of metal powders results in a large volume increase. Dr. Duwez illustrated this point nicely in Au-Cu at the Powder Metallurgy Symposium sponsored by Sylvania last summer. When the alloy is first forming, beryllium diffuses into the zirconium and two things occur which can increase the volume: (1) The resultant Be-Zr phase formed is of greater volume than that occupied by the zirconium and growth occurs in this region. (2) Pores are left where the beryllium had been, separating the alloy particles, and thus making it unfavorable for subsequent diffusion of the alloy and coincident densification. The alloy particles may in themselves be more dense than the mixture, but gross density of the compacts were measured, and this shows a low density. On reheating the pressed alloy powder at a higher temperature further alloy formation is very limited. In fact the original beryllium and zirconium are gone prior to this operation and only a closer approach to equilibrium occurs. Even so sintering was poor because the diffusion rate must be low in the alloy mixture and only the earliest stages of sintering have occurred. Thus the melting point of this alloy must be well above 1350°C. There is no discrepancy in the two statements "growth of the alloy indicates formation of a high melting phase . . ." and "even at 1350°C, no indications of sintering have been observed." The term "sintering" was here used to connote a gross densification and coincident shrinkage of pores. The high-melting point phase formed by diffusion in the solid state alone. Sintering did not occur because the resultant compact from such treatment was even more friable and less dense (gross density) than in the pressed state.

5. The mixing was such, as explained in point 2, that no gross separation could have occurred prior to sintering. No other explanation than the one given for this structural difference from top to bottom of the sample seems plausible.

6. We do not believe that the composition from top to bottom is much different, but that the bottom portions are more like a 3 or 4 pct Be composition and the top portions perhaps like a 6 or 7 pct Be composition. The sample may not have been completely molten and more solid zirconium particles tended to remain in the bottom of the mushy sample.

7. Figs. 9 and 10 were included to show the basic zirconium and beryllium structures. It is difficult to see the eta phase which should be present in fig. 10 and this micrograph looks very much like sintered beryllium.

8. Referring to the 20 pct Be composition, it is true that the reaction appears to be partial, but the microstructures do not tell the entire story. The compacts were friable after heating at the lower temperature and these microstructures are difficult to interpret. The partial melting which occurred at 1350°C gave us a more dense compact from which we could get a good microstructure, but the X-ray evidence, table II, shows that there is no difference between heating at 1100° or 1350°C in the phases present. The samples only look different because one is solid while the other consists of a rather friable powder.

9. Many large pores, voids, and cracks are visible in the 60 pct Be mixture. In fig. 19 some of these may appear to be a second phase, but closer examination under the microscope clearly reveals this as a single-phase structure with many tiny cracks throughout the matrix.

10. More precisely our statement should have been that the eta phase is probably an intermetallic compound, and the product of a peritectic or monotectic reaction.

11. The reasoning that the beta-to-alpha transformation should be lowered seems good. It is, then, probably better to assume a eutectic reaction with beta → alpha + gamma (fig. 25).

12. The apparent difference in the amount of eta phase seen in the micrographs and that expected from the lever rule may in part be explained by the large difference in density of the two components. The density of Be is 1.85 g per cm^3. A 40 pct Zr-60 pct Be mixture pressed, heated 2 hr at 1100°C, powdered, pressed, and sintered 4 hr at 1350°C had a density of 2.31. This sample contained many voids and it may be

assumed that the true density of such a composition is even higher. The volume percent (which corresponds to area percent on a random cut) is thus considerably less than the weight percent expected. Thus amounts of eta phase seen in micrographs of 80, 90 and 95 pct Be should be perhaps about 30, 20 and 10 pct, or even less, of the total area. The eta phase may, however, vary in composition even more than is shown in the hypothetical phase diagram.

I should like to thank Dr. Hansen again for the splendid discussion he has prepared. He has brought out many interesting concepts some of which we were not entirely aware. Such discussion helps to clarify many points which are not immediately clear in a preliminary work and should benefit those who investigate this system more thoroughly in the future.

Cemented Titanium Carbide

by J. C. Redmond and E. N. Smith

DISCUSSION, S. Tour presiding

S. J. Sindeband—I should like to ask a number of questions with regard to this excellent and informative paper:

The method for determining the compressive strength of the specimens is apparently one communicated privately by Dr. Bridgman. I wonder if it would be possible for the authors to indicate some of the details of this method.

In the apparatus for measuring the hot transverse rupture properties, what material was used in the ⅛ in. cylinders and the 10 mm ball?

In table II, the relative degree of corrosion of various titanium carbide compositions was shown. However, in the text which follows the discussion of table II, it was indicated that the variety of supports employed affected the rates of corrosion observed for many compositions. What kind of supports were used for the specimens described in table II? From the data shown graphically in fig. 4, one might expect that carbon supports were used. If this was not the case, and ceramic supports were used, table II would seem to contradict fig. 4. In addition, the same question is advanced regarding table III, where the results of the 210-hr oxidation test are given. Once again, I wonder what variety of supports were employed.

Since the measurement of corrosion was one of thickness increase and not of gain in weight, the variation in performance of carbon supports and ceramic supports could not be due to reactions at the point of contact. I wonder if any study was made of the atmosphere composition prevailing in the unsealed muffle for each of these conditions.

I was interested to note the comparison between milling with WC balls and steel balls, and wonder, if 3 pct W was picked up in the first case, what the quantitative amount of iron was where the steel balls were employed. The transverse rupture stress obtained for the compositions reported upon compares very favorably with previous data on TiC compositions, and I wonder if the author would care to make any comment to indicate to what he attributes the improvements.

C. G. Goetzel—The authors are to be congratulated for the performance of this excellent piece of metallurgical research, and, what appears almost more commendable, for their frank and detailed discussion of procedures used and results obtained. This work may well be considered a milestone in the development of new and better materials of construction, especially as they relate to applications involving operation at very high temperatures. Titanium carbide, by virtue of its so interesting combination of physical and chemical properties, appears destined to play an important, if not dominant, role in this new materials progress.

Of particular interest appear the results connected with the multicarbide compositions containing the CbC-TaC-TiC solid solution. The authors mention that this solid solution was made by the McKenna "menstruum" process. Were any tests made with solid solution carbides of the same composition that were prepared by other, i.e., more conventional methods, such as diffusion treatment of mixtures of the carbide components, or the joint carburization of mixtures of the component oxides? It would be interesting to note whether a similar improvement in the high-temperature oxidation resistance would result, and whether this, too, would be accompanied by a sacrifice in transverse rupture strength of over 20 pct at 1800°F, as compared with the plain TiC-base compositions. In this connection, it is worthwhile noting that a relation between transverse rupture and stress rupture strength for the cemented titanium carbides is still missing, and final conclusions as to the high-temperature strength characteristics of the material must be reserved.

The procedure selected by the authors for establishing the resistance to high-temperature oxidation is novel and requires checking against other methods conventionally used in high-temperature materials work. Since the increase in thickness is a function of the material composition, the results obtained by such measurements appear not strictly comparable for different compositions. It would be helpful for a full evaluation of the test results if comparison data were given for the change in weight reduced to the exposed surface area, possibly both, for exposure to still air and to an air stream at the test temperature. The reduction in strength of the test specimen after exposure appears to be a good indication of the order of impairment caused by oxidation, but leaves open the question of the extent of deterioration of the apparently healthy core, e.g., by diffusion of the oxygen along the grain boundaries. The method employed by National Advisory Committee for Aeronautics[14] of grinding off the oxide layers on two opposite parallel faces and measuring microscopically the thickness of the remaining unimpaired cross-section appears to be a more direct approach to the problem.

The authors' description of the microstructure is not clear to the writer. A comparison of fig. 10 with fig. 9 does not only fail to show a larger grain size of the material containing CbC and TaC, but actually gives the impression of the reverse effect. The statement that there appears to be no significant change in structure after 210-hr exposure at 1800°F is not borne out by the two micrographs of figs. 10 and 11, which show a very marked contrast indeed. Fig. 11 indicates, at least in the writer's mind, a noticeably progressed deterioration of the binder phase, and possibly also of the surface areas of the carbide grains.

J. C. Redmond and **E. N. Smith** (authors' reply)—In reply to Dr. Sindeband's questions, the important feature of the method of Bridgman used for determining the compressive strength, lies in the use of a special fixture to assure alignment. A ¼ in. diam x ¼ in. high specimen is used. The anvils between which the specimen is crushed are of cemented tungsten carbide supported by shrunk on heat-treated high-speed steel bands. Heat-treated high-speed steel rams apply the testing machine force to the anvils. The anvil and ram pieces are lapped to fit into a heat-treated outer steel sleeve. Centering washers are used to keep the specimen in the center of the anvils. We have also found that thin copper shims used between the ends of the specimens and the anvils eliminate spalling.

The cylinders and the ball used for the hot trans-

S. J. SINDEBAND, American Electro Metal Corp., Yonkers, N. Y.; C. G. GOETZEL, Sintercast Corp. of America, New York, N. Y.

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[14] M. J. Whitman and A. J. Repko: Oxidation of Titanium Carbide Base Ceramals Containing Molybdenum, Tungsten, and Cobalt. National Advisory Committee for Aeronautics. *Technical Note* 1914.

verse rupture test apparatus were of cemented titanium carbide.

With regard to the type of supports used in the various oxidation tests, it does not appear to us that there is any contradiction between table II and fig. 4, although as a matter of fact carbon supports were used in the 18 hr tests. It should be noted that TaC does not behave quite the same as the combination. In the 210 hr tests, ceramic supports were used, and there is some inconsistency. However, the results still demonstrate the marked superiority of the compositions containing columbium and tantalum over those using only TiC and an auxiliary metal.

No analyses of the muffle atmosphere were made. The iron pickup amounted to only 2 to 3 pct when steel balls were used, and this we did not consider significant in view of the fairly high strengths attainable with iron alone.

With regard to the reasons for the improved transverse rupture strength, one important factor is undoubtedly the titanium carbide which was used. The methods of making the titanium carbide employed in compositions reported in the past undoubtedly produced a carbide containing more or less free carbon and other impurities. Improved processes have been developed for making the carbides and for all steps of producing the compositions.

In reply to Dr. Goetzel's question no compositions containing titanium, columbium, and tantalum carbides have been made starting with the three individual carbides. Provided all three of the carbides were available in pure form we do not believe the results would be appreciably different than when using the three-carbide solid solution.

No entirely satisfactory method for measuring rate of oxidation of these materials is available, as discussed in the paper. The measurement of the increase in weight is subject to the same difficulties of effect of variation in composition as is the measurement of the thickness increase. Methods based on the removal of the coating are subject to difficulties especially when very thin coatings are involved.

There is a tendency toward larger grain size of the compositions containing columbium and tantalum, which in part answers Dr. Goetzel's question with regard to figs. 9 and 10. The larger grain size does exist and is best observed by examining many specimens.

There is evidence of deterioration of the auxiliary metal phase in fig. 11 as mentioned by Dr. Goetzel, but the skeleton appears intact and the grain size has not increased. Recent work has indicated the strengths do not decrease with the changes observed.

Stress-rupture tests are desirable and preliminary values have been recently obtained. They indicate far greater life at 1800°F than for alloys. Final results will not be available for some time.

The Elastic Coefficients of Single Crystals of Alpha Brass

by R. W. Fenn, Jr., W. R. Hibbard, Jr., and H. A. Lepper, Jr.

DISCUSSION, R. Smoluchowski presiding

H. E. Stauss—The authors have chosen to measure the elastic properties by a "static" method. Such a method gives elastic constants that on the average for most metals are about 10 pct less than values obtained by "dynamic" means. Which type of value would the authors consider more correct?

R. W. Fenn, Jr. (authors' reply)—The authors were unaware of the discrepancies Dr. Stauss speaks of. It is hoped that he will publish any new data he has in the near future. In general, greater accuracy is available from the dynamic methods. For details see Hearmon.[9]

H. E. STAUSS, Naval Research Laboratory, Washington, D. C.

Behavior of Pores during the Sintering of Copper Compacts

by F. N. Rhines, C. E. Birchenall, and L. A. Hughes

DISCUSSION, J. C. Redmond presiding

A. J. Shaler—I should like to congratulate the authors on the presentation of this paper, which we have been awaiting a long time.

The view they have taken of the sintering process, namely that voids are comparable to particles of a second phase capable of dissolving to a slight extent in the metal phase, is an interesting but dangerous one. Pines has given a first-order solution of the problem and has predicted a decrease in the concentration of pores near the surface. The authors of the present paper have experimentally demonstrated the second-order effects, that is, the diffusion of the space phase between voids of different sizes, and also the movement of atoms from highly curved parts of a void to less curved regions of the same void. I have recently calculated the rate of vapor-phase transport within odd-shaped pores in copper at 850°C and found that probably at that temperature volume flow is the more rapid shape-changing mechanism. The authors of the present paper have found that at 1000°C, vapor-phase transport is dominant. There is no disagreement here, I think. The dominant phenomenon can easily be different in different temperature ranges and with different pore shapes: I used a cylinder going to a sphere, not a tricuspid going to a "triple cuspidor."

A. J. SHALER, Massachusetts Institute of Technology, Cambridge, Mass.

But there is some danger in the other part of the explanation, that is, in the study of the diffusion of vacancies from a pore to its neighbors and to the outside. A vacancy is very different in dimension from an atom. When it moves, it carries a field of elastic strain. This has to be taken into account. A concentration gradient of vacancies can cause them to diffuse. But in the absence of such a gradient, they can be made to diffuse by a field of stress.

What happens in some of our experiments, and it is most noticeable in the shrinkage of synthetic cylindrical pores, like the tubes we have been working with, may be broken down into the following steps. (1) The presence of a surface establishes a vacancy concentration gradient, as Dr. Kuczynski and the present authors have shown. (2) Vacancies then diffuse in order to decrease this gradient. (3) In so doing, they cause an elastic field to be built up in such a direction as to oppose the diffusion, so that it slows down until it reaches a steady-state rate. (4) The steady-state flow is due to the fact that the surface tension acting on curved surfaces applies a stress to the system which itself mechanically causes vacancy diffusion. What I have said is that the diffusive types of flow of the authors and of Dr. Kuczynski are transient phenomena which soon stop if the pores are large. We are then left with a mechanical problem only, and our researches have not yet disclosed just what the mechanism of flow is; it may be a slip process, or it may take place by a vacancy diffusion of the type Nabarro has described. It appears to be a viscous flow in the sense that the strain-rate is proportional to the stress. In any case, it is a mechanical problem.

G. C. Kuczynski—The authors in choosing for this work powders with particles of irregular shape and wide size distribution should have realized in advance, I believe, that their experimental findings would be very difficult to check with any theory because of necessary approximations which must be made in developing a theory to fit the complicated geometry. Knowing as little about the mechanism of densification as we presently know it would be advisable to keep as many variables as possible constant during the experiment. An ideal solution should be to establish the relationship between the radius of uniform sized pores and time.

The whole weight of the experimental work presented here seems to be concentrated upon the construction of the space diagram showing the population distribution of pores of various sizes as a function of time at given temperature. We know, of course, that if we can make a correct count of the population distribution of pores of different sizes in a compact, we can very simply calculate the total pore volume and hence the compact density. If the densities calculated from the pore count do not agree with the measured densities, obviously we must consider the counts in error and can therefore base no further conclusions upon such counts. The comparison of the measured and computed densities in table VI shows clearly that the counts cannot be adequate as the densities calculated from them hardly change with time.

It is obvious that the discrepancies revealed in table VI invalidate the space diagram in fig. 8, which is the core of the work.

With the greatest interest I read that the authors observed a completely densified layer on the surface. I should be very indebted to them if they could give some more information about it, such as its thickness as a function of time and temperature. If this information was available, it would be possible to attempt to evaluate the self-diffusion coefficient and throw some light upon the mechanism of densification.

Passing now to the theoretical part I should like to mention that the first to propose the diffusion theory of densification of the powder compounds was Pines. His paper was published in Russian and has been available in English translation since 1946.[17] Treating the voids as sources, Pines was able to solve the Laplace equation with source intensities and obtain the expression for shrinkage of the compacts in terms of diffusion coefficient. He also predicted that in certain cases, namely when the specimens are too big, the sintering is not uniform but first takes place on the surface.

It is, however, not altogether certain that a diffusion mechanism can account for the shrinkage of the compact in the observed short period of time. A simple calculation shows that if the excess concentration of vacancies in Cu at 1000°C is produced by pores of 1 micron radius and diffusion has to take place over a path of 1 mm then the decrease of linear dimensions due to volume diffusion will only be $3\text{x}10^{-6}$ cm per day, which falls far below the observed rates. Moreover the sintering rate would be a function of the shape and size of the compact. It is true that we do not have enough experimental evidence to accept or refute even this statement, but it does not seem likely.

Mackenzie and Shuttleworth[18] maintain that the densification mechanism is that of plastic flow. The present investigation does not offer any clear-cut solution, because all the observations reported by the authors may fit into plastic flow as well as diffusion theory. The question what mechanism is responsible for the densification of powder compacts is still left open.

It seems to me that in order to decide this question a very simplified experiment would have to be performed before we can tackle with any sense, the analytically difficult problem of powder compact.

Closing my comments I should be grateful to the authors for the details of the computations leading to the figures listed in tables VIII and IX. This would be of interest because, although the measured and computed porosities (from table VI) differ only by as much as 360 pct, the measured and calculated rates of density changes (tables VIII and IX) differ by as much as 100,000 pct.

F. N. Rhines, C. E. Birchenall, and **L. A. Hughes** (authors' reply)—The authors wish to thank Messrs. Shaler and Kuczynski for their thoughtful and thought provoking comments. We cannot but agree with both that the subject is by no means closed. Indeed, it appears unlikely that the mechanism of sintering can be clearly stated, or proved, until the nature of the diffusion process itself is better understood.

In specific reply to Dr. Kuczynski's questions, it should be pointed out that the density cannot be computed directly from the pore count in a case, such as the present one, for two important reasons. First, the pore shape is unknown during most of the process, and second, there is a wide diversity in pore shape until very late in the sintering process, when the spherical form, or something rather close to it, is approached by all pores. As has been shown in the paper, it is possible to show correlation between the measured density and the pore count by assuming different pore shapes at various times during the process, but this is a highly artificial procedure and of doubtful significance, for the reasons just cited.

Concerning the question of more rapid sintering at surfaces, some additional detail may be of interest. There is no sharply defined band, next to the surface, which is free from pores. However, the pore distribution adjacent to the surface is such that none either penetrate the surface or occur within a pore diameter of the surface. Also there is a striking absence of small pores near the surface; such pores as do occur in this area are mostly of the large (most stable) sizes. Thus, it appears that there is a marked tendency for sintering to go to completion first at the external surface.

Referring to the 1000°C, 1-hr conditions, if one assumes the theoretical density of copper to be 8.96, the measured porosity is 1900 pct greater than that computed from the pore count assuming spherical shape. This is, of course, very different than the 10^3 discrepancy in measured and computed values (a step by step description of this procedure is given in the paper beginning with the second paragraph on p. 385). Even before the presentation, the authors had modified their views somewhat and suspected that a great part of the early densification occurs through the nearly continuous paths of bridges between powder particles which are not yet soundly formed throughout the mass.

It still seems to the authors that the presence of elastic strains (surface tensions) in the neighborhood of a source of vacancies (pore or surface) should be enough provocation for the formation of a vacancy concentration different than the normal equilibrium value. There also seems little reason to expect the dimensions of a vacancy in a sintering compact to be appreciably different from a vacancy in a solid piece of metal on which self-diffusion rates are measured. It appears to the authors that the areas of agreement with Dr. Shaler may greatly exceed the differences when we become more accustomed to each other's terminology.

As a result of these discussions, it is evident that a critical contribution would be the demonstration that sintering is, or is not, size and shape dependent. It is rather surprising that at such a late date this is not one of the sure facts of the field.

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[17] Pines: *Sci. Pub.* Ukrain. Phys. Tech. Inst. of State Univ. Jan. 15, 1946.

[18] Mackenzie and Shuttleworth: *Proceedings.* Physics Society. (London) (Nov. 1949).

Self-Diffusion in Alpha and Gamma Iron

by C. E. Birchenall and R. F. Mehl

DISCUSSION, M. B. Bever presiding

R. E. Hoffman and **D. Turnbull**—The authors have presented evidence which they have interpreted as indicating that the rate of self diffusion is not intrinsically more rapid at grain boundaries than within the grain. Grain-size effects which apparently exist are attributed rather to impurities concentrated at the grain boundaries. In view of our own experiments and the existing evidence, we believe that the support for this hypothesis is not convincing.

We have in progress an investigation in which the rate of self diffusion of silver is being measured over an extended temperature range in both single-crystal and polycrystalline specimens. The results of the single-crystal experiments and some preliminary data on fine-grained polycrystalline specimens have already been reported,[24] and it is anticipated that a complete report will be published in the near future.

The self-diffusion coefficient of large-grained polycrystalline silver (1 grain per sq mm) has previously been measured by Johnson[25] between 730° and 940°C. The diffusion coefficients which we have measured in single crystals (210 plane normal to diffusion direction) agree within experimental error with values calculated from an extrapolation of Johnson's curve down to temperatures as low as 500°C. However, it has been demonstrated that the overall self-diffusion rate in fine-grained polycrystalline specimens (initial grain size of 0.003 cm) becomes measurably larger than the overall rate in a single crystal at a temperature of 600°C, and the discrepancy between the two rates becomes greater as the temperature is further decreased. In fact, it has been possible to obtain satisfactory penetration curves for polycrystalline specimens using the sectioning technique at temperatures as low as 400°C. At this temperature, the penetration is 50 to 100 times greater in the polycrystalline specimens than in a single crystal.

Fisher[26] has developed an analysis whereby the ratio of the rate of the unit diffusion process at the grain boundary to the corresponding rate within the grain can be calculated from the penetration curves and an assumption as to the width of a grain boundary. This analysis applied to our data indicates that the unit process at the grain boundary is faster by a factor of 10^6 at 475°C when the grain boundary width is taken to be 5Å.

The silver used in most of these experiments was obtained from the Handy and Harmon Co. and listed as 99.97 pct pure. Preliminary experiments on 99.999 pct silver from the Jarrel-Asch Co. indicate a grain-size effect of the same order of magnitude as in the less pure silver. Nominally, these purities are as good, at least, as that of the carbonyl iron used by the authors, but of course if an impurity effect does exist its magnitude might be very dependent upon the nature of both major and minor constituents.

The authors have cited the work of other investigators who have found no grain-size effects. Neither Steigman, Shockley and Nix[8] nor Maier and Nelson[8] were able to correlate self-diffusion coefficients of copper with grain size. However, all their measurements were performed at or above 750°C; and on the basis of our work with silver, no grain-size effect would be expected at temperatures above about 0.7 of the absolute melting temperature unless the grain size were exceedingly small. Likewise, in the investigation of the self diffusion of lead by Seith and Keil,[14] the lowest temperature at which the diffusion coefficient was measured in polycrystalline specimens was 207°C, which is still sufficiently high so that the lack of a grain-size effect is not surprising. Finally, in those experiments on iron from which they concluded that there was no grain size effect, Drs. Birchenall and Mehl seem to have no information as to the actual grain sizes immediately prior to and following the diffusion anneal. Without this information, we believe that their own experiments offer little support for their hypothesis.

F. S. Buffington, I. D. Bakalar, and **M. Cohen**—The results given in this paper agree in order of magnitude with those tentatively reported by us.[27] However, significant differences exist in the two sets of data, and it may be well to make an explicit comparison. The diffusion studies at M.I.T. were conducted on somewhat higher purity iron (99.98 pct Fe) than the grades used by the authors, but this is undoubtedly not the answer.

Fig. 4 shows the diffusion results of both laboratories for the gamma phase, omitting the authors' data on the commercial steels, while fig. 5 presents a similar comparison for the alpha phase. The divergence is much more marked in the latter case than in the former. In connection with the M.I.T. determinations, all of the runs in the gamma range and those above 800°C in the alpha range were conducted with specimens having a relatively thick (0.002 cm) electrodeposit of radioactive iron. This practice minimizes any possible error due to extraneous diffusion that may occur during the heating to and cooling from the operating temperature. An exact solution of Fick's law for these boundary conditions was used in calculating the diffusion coefficients.

At a later time, three runs were made below 800°C, using very thin electrodeposits similar to those of the authors, and the points fell considerably below the values expected from the extrapolation of the results based on the specimens with the thick deposits (compare dash-dot line in fig. 5). However, in the runs with the thin deposits, deviations of 100 pct were found between the individual specimens, whereas the maximum deviation with the thick deposits was less than 25 pct. Accordingly, it is not known at the moment whether the M.I.T. points below 800°C should be given as much weight as those above 800°C. If this were done, the frequency factor would be of the order of 400 cm^2 per sec, which is quite high. In other metals, the frequency factor for self diffusion lies between about 0.1 and 10 cm^2 per sec. As the points below

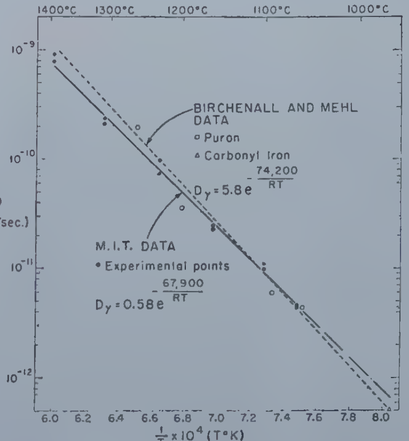

Fig. 4—Self-diffusion of gamma iron.

R. E. HOFFMAN and D. TURNBULL, General Electric Co., Schenectady, N. Y.; F. S. BUFFINGTON, I. D. BAKALAR, and M. COHEN, Massachusetts Institute of Technology, Cambridge, Mass.

800°C stand now, they fall closer to the authors' plot than to the M.I.T. plot.

To resolve this issue, we are now carrying out diffusion runs in the delta-phase range, with a sectioning-type of specimen. At 1425°C, the M.I.T. equation predicts a diffusion coefficient of 1.2×10^{-7} cm^2 per sec while the authors' equation predicts a value of 8.7×10^{-7} cm^2 per sec. Actual experiments in the delta phase should show whether the present disagreement is due to a difference in techniques (thin deposits vs. thick deposits), or whether the experimental error of both techniques is so large that all the data should be averaged to obtain the best straight-line plot. If the latter turns out to be the case, the data from the two laboratories for the gamma phase in fig. 4 should be similarly averaged. The results of the proposed runs in the delta region will be available soon, and will be published in the form of a Technical Note.

C. E. Birchenall and **R. F. Mehl** (authors' reply)—We wish to thank the discussers for their comments and welcome this opportunity to say more about the low temperature part of the alpha iron self-diffusion curve to which both discussions relate. Perhaps the problem can be seen most clearly by reference to fig. 5. It is apparent that the agreement of the two independently determined sets of data is within the experimental scatter over the whole of the alpha range. However, it is not possible to draw any single straight line through the data on a log D vs. $1/T$ plot which is in satisfactory agreement with the points. The deviations are just the opposite of those to be expected as a result of grain boundary diffusion. More recent runs at still lower temperatures seem to indicate a continuation of that trend. If it is assumed with Hoffman and Turnbull that grain boundary diffusion is much more rapid than volume diffusion in both our carbonyl iron and Buffington, Bakalar, and Cohen's 99.98 pct Fe, these deviations must become even greater than shown. This is possible, of course, and neither set of data seem complete enough to exclude it. A few experiments are planned to test this point specifically.

However, the major point of this very tentative suggestion was that some grain boundaries in systems containing an appreciable concentration of a second component may differ from those in a very pure metal. Thus the assumption of a constant 5 Å width in Dr. Fischer's unpublished analysis of grain boundary diffusion may be applicable to an average grain boundary in pure silver, but it may have little to do with self diffusion of iron at low temperatures in commercial iron sheet with more than 0.4 pct impurities and even less to do with diffusion in a 30 pct Zn-70 pct Cu pure copper couple at the low temperatures where grain boundary diffusion is important.

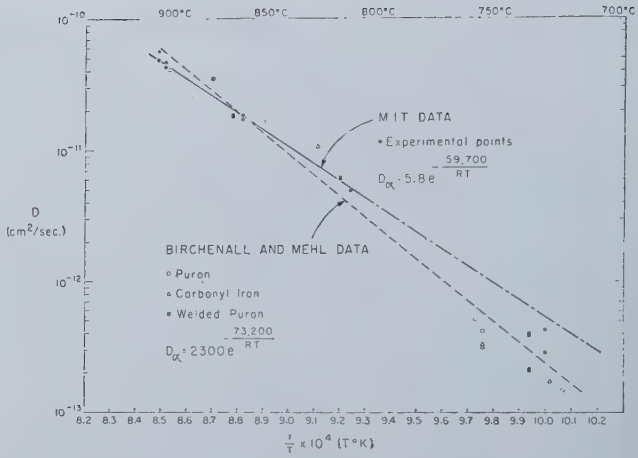

Fig. 5—Self-diffusion of alpha iron.

Extension of arguments based on the magic number 0.7 T_m obtained experimentally for silver and inferred for lead and copper should certainly be restricted to f.c.c. metals. The effect is not to be found in b.c.c. iron at 0.61 T_m.

Without some such behavior as that postulated, it would seem impossible to continue to ascribe the anelastic effects associated with grain boundaries to grain boundary diffusion processes.[16] A comparison of the effects of impurities on both diffusion rates and anelastic properties might give an answer to this.

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[25] W. A. Johnson: *Trans.* AIME (1941) **143**, 107.
[26] J. C. Fisher. To be published.
[27] Physics of Sintering. Sylvania Conference 1949. McGraw-Hill Book Co.

Diffusion Coefficient of Carbon in Austenite

by C. Wells, W. Batz, and R. F. Mehl

DISCUSSION, J. H. Hollomon presiding

L. S. Darken—It is indeed gratifying to find that the results of the two different methods here reported are in substantial agreement with each other and with the earlier work[1] of two of the authors.

Dr. R. P. Smith, of our laboratory, has been conducting some experiments at 1000°C to determine the diffusivity of carbon in austenite by a third method—the steady state method. This work, which will soon be reported, is far enough advanced that we can say it is in substantial agreement with that of the present authors. The only disparity which might be considered significant is in the high-carbon region, where we find that the diffusivity rises a little less steeply than indicated in fig. 8.

F. E. Harris—The authors have presented an impressive arrangement of data concerning the diffusion of carbon in austenite. Of particular interest is the compilation, table IV, which is repeated in col. *B* of table V for direct comparison with values (col. *A*, table V) from a formulation using a single Q value of 31,000 cal as the activation energy for diffusion.

This comparatively simple formulation has been used quite successfully in the practical application of calculating the carbon added (or removed) through the face in carburizing and decarburizing experiments, where the face concentrations are held quite constant for known times and temperatures. Literally hundreds of tests have been so checked where the computed and experimental values have varied by less than 5 pct. For higher temperatures, where proper carburizing data are hard to obtain, the diffusion couple is treated as a decarburization of the high-concentration bar and as a carburization of the low-carbon member. The analysis has been limited to a maximum of 1.40 wt pct carbon.

The agreement between cols. *A* and *B* in table V may be considered fair, if a liberal viewpoint is taken. The use of a diffusion couple has one serious drawback, in that comparatively small amounts of carbon pass through planes of concentration close to those of the initial high-carbon and low-carbon members, and hence small errors become important. In addition to the sensitivity at these high and low concentrations,

L. S. DARKEN, U. S. Steel Corp. Research Lab., Kearny, N. J.; F. E. HARRIS, Buick Motor Div., General Motors Corp., Flint, Mich.

Table V. Comparison of Calculated and Experimental Amounts of Diffusion of Carbon

°C	$D_0 x 10^7$	0.22 Wt Pct C		0.44 Wt Pct C		0.66 Wt Pct C		0.88 Wt Pct C		1.12 Wt Pct C		1.35 Wt Pct C	
		A	*B*	*A*	*B*	*A*	*B*	*A*	*B*	*A*	*B*	*A*	*B*
750	0.0734					0.178	0.18						
754	0.0779					0.188	0.20						
800	0.1495			0.291	0.27	0.362	0.35	0.432	0.52				
802	0.1535			0.300	0.30	0.371	0.41	0.700	0.63				
847	0.2751	0.405	0.35	0.535	0.39	0.665	0.44	0.796	0.56				
848	0.2787	0.410	0.27	0.542	0.36	0.674	0.47	0.806	0.67				
905	0.5465	0.805	0.82	1.06	1.03	1.32	1.33	1.58	1.54	1.86	1.95		
909	0.5716	0.842	0.98	1.11	1.13	1.38	1.35	1.65	1.71	1.95	2.98		
910	0.5778	0.851	0.87	1.12	0.98	1.40	1.23	1.77	1.54	1.97	2.26		
916	0.6188							1.79	1.63	2.11	3.16		
950	0.8897	1.31	1.74	1.73	2.15	2.15	2.66	2.57	3.27	3.03	4.09		
956	0.9471	1.40	1.89	1.84	2.20	2.29	2.56	2.74	3.07	3.23	4.09		
958	0.9669	1.43	1.33	1.88	1.74	2.34	2.15	2.80	2.76	3.26	3.99		
999	1.454	2.14	3.48	2.83	4.10	3.52	4.71	4.20	5.43	4.96	6.66	5.67	12.29
1,000	1.464	2.16	2.87	2.85	3.48	3.54	4.40	4.23	5.63	4.99	7.17	5.71	10.03
1,005	1.541	2.27	2.71	3.00	3.09	3.73	3.74	4.46	4.73	5.25	6.25	6.01	8.50
1,010	1.617	2.38	3.48	3.15	3.99	3.91	4.81	4.68	6.04	5.51	7.89	6.31	10.24
1,038	2.096	3.09	3.69	4.08	4.20	5.07	4.72	6.06	5.44	5.51	6.46	8.18	8.00
1,042	2.173	3.20	4.92	4.23	5.54	5.26	6.36	6.28	7.49	7.41	8.92	8.48	11.08
1,127	4.467	6.58	12.35	8.67	13.38	10.8	14.72	12.9	16.47	15.2	19.66	17.4	24.91
1,128	4.501	6.63	10.81	8.76	12.35	10.9	13.89	13.0	15.95	15.3	19.04	17.6	26.45
1,195	7.487	11.0	19.41	14.7	21.16	18.1	23.12	21.7	25.81	25.5	30.97	29.2	42.53
1,195	7.487	11.0	18.79	14.7	21.26	18.1	23.74	21.7	26.63	25.5	30.97	29.2	41.29
1,255	11.37	16.7	27.96	22.1	30.03	27.5	32.10	32.9	35.20	38.7	40.38	44.4	55.91
1,301	15.32	22.6	29.06	29.8	33.21	37.1	39.44	44.3	55.00				
1,305	15.70	23.1	33.22	30.6	36.33	38.0	41.00	45.4	48.37	53.5	57.30		

$D_o = 0.031\ e^{-\frac{31{,}000}{RT}}$ cm² per sec

$D = D_o\ (1 + 2.15 \times \text{wt pct C})$
$A = 1.473\ D_o \cdot 10^7$ for 0.22 wt pct C
$A = 1.946\ D_o \cdot 10^7$ for 0.44 wt pct C
$A = 2.419\ D_o \cdot 10^7$ for 0.66 wt pct C
$A = 2.892\ D_o \cdot 10^7$ for 0.88 wt pct C
$A = 3.408\ D_o \cdot 10^7$ for 1.12 wt pct C
$A = 3.903\ D_o \cdot 10^7$ for 1.35 wt pct C
B values are taken from table IV.

the method which the authors employ in evaluating *D* is, in my opinion, particularly in error for these boundary concentrations, and there is reason to believe that the *D* values so obtained are consistently too large for the end concentrations of a given couple.

C. Wells, W. Batz, and **R. F. Mehl** (authors' reply)—The confirmation of the results in this paper by Dr. Smith's steady-state method for determining the diffusivity of carbon in austenite is satisfying. The authors wish to remind Dr. Harris that the experimental results in this investigation have been verified to be correct within experimental error by three methods: two reported in the paper and the steady-state method of Dr. R. P. Smith, which shows only small discrepancies in the high-carbon region.

The Growth of Austenite as Related to Prior Structure

by A. E. Nehrenberg

DISCUSSION, J. H. Hollomon presiding

R. A. Schmucker, Jr.—The writer wishes to point out that an acicular growth of austenite, similar to that described in the author's paper, was recently observed in an alloy steel of only 0.06 C content. This steel, which represents an 0.07 max C, 1.35 Cr, 0.55 Ni, 0.20 Mo analysis, combines the characteristics of minimum hardness in the annealed condition with maximum hardenability and is therefore suited primarily for cold-hobbing applications. The acicular austenite formation in this steel was observed accidentally during a determination of its Ac_1 temperature.

The samples used in this investigation represented as-forged bar stock which had been given a preliminary temper at 1300°F. The critical (Ac_1) temperature was finally established at 1400°F. Fig. 15 represents the microstructure of the sample which had been heated at 1450°F for ½ hr, water quenched, and tempered at 600°F for ½ hr (for the purpose of darkening the martensite). It will be observed from the distribution of the darkened areas of martensite that the parent austenite grains formed at 1450°F had grown in an acicular manner and still occupied only a small percentage of the total area. The remainder of the area contains the original equiaxed ferrite grains in which new austenite had as yet scarcely formed. However, the tiny isolated martensitic patches at several points where three or more ferrite grains intersect indicate that small austenite grains had formed and started to grow in an apparently equiaxed fashion.

Fig. 16 represents the prior microstructure of an original sample in the as-forged and tempered condition, before it was heated above the critical temperature. It is probable that there are two kinds of ferrite in this structure: (1) The equiaxed proeutectoid ferrite grains which separated from the austenite when the steel was cooled from the forging temperature, and (2) the acicular ferrite associated with the aggregate of fine carbide which is represented by the patches of

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R. A. SCHMUCKER, JR., Crucible Steel Co. of America, Harrison, N. J.; A. HULTGREN, Royal Institute of Technology, Stockholm, Sweden; J. R. VILELLA and R. A. GRANGE, U. S. Steel Corp. Research Lab., Kearny, N. J.; O. ZMESKAL, Illinois Institute of Technology, Chicago, Ill.

darker etching structure grouped near the center of the micrograph. According to the author's view, these acicular grains of ferrite would have formed when the martensite or bainite in the as-forged structure was tempered. Regardless of the theory of the acicular ferrite grains, it appears quite conclusive from a comparison of the two micrographs that the acicular growth of new austenite grains represented in fig. 15 took place only in those areas which were occupied by the agglomerated acicular transformation product in fig. 16. There is also some evidence from the incipient growth of austenite in the equiaxed ferrite in fig. 15 that the new austenite grains are correspondingly equiaxed.

A. Hultgren—In fig. 14 the author demonstrates how, during heating of a hypoeutectoid alloy steel 4140, the last ferrite to transform is located in areas formerly occupied by pearlite. Among the excellent micrographs of this paper, there are several others that illustrate the same phenomenon. Fig. 3*a* shows that, on heating the same steel, previously hardened and tempered, to 1420°F, the ferrite areas still untransformed contain no carbide, although such particles very likely were present in those areas before austenite formed, as indicated by the structure shown for 1360°F. A similar conclusion may be drawn from fig. 3*b* where the prior structure was obtained by a spheroidizing anneal not involving hardening. In fig. 11 (steel 4140) the small ferrite areas remaining at 1450°F lack carbide particles, whereas a large one contains such particles only in its central portion.

Hence it may be concluded that, on suitably slow heating of a hypoeutectoid steel of any prior structure, at least for certain alloy compositions, a stage is reached where the austenite formed still retains a fair amount of carbide particles or lamellae, whereas untransformed areas are ferrite free from carbide. The carbide missing in those ferrite areas appears to have been dissolved in the ferrite matrix. The following explanation of this phenomenon is suggested. For simplicity, only the case of a hypoeutectoid carbon steel will be considered, although it may be suspected that certain alloy elements play a significant part in the reaction.

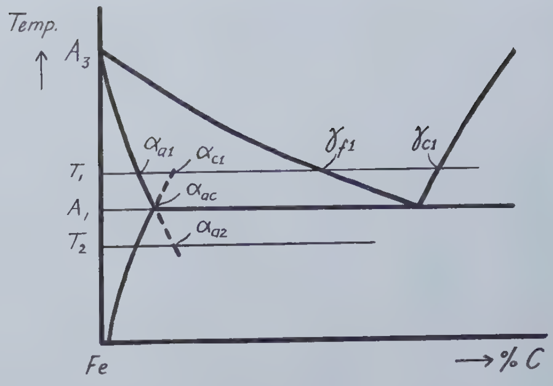


Fig. 17—Portion of equilibrium diagram to illustrate change in carbide solubility.

The underlying assumption of the following reasoning is that whenever two phases touch there will be a reaction between them at the interface towards establishing in the contacting layers the equilibrium compositions for those two phases at the temperature in question.

It is well known,[19, 20] although still not satisfactorily explained, that when pearlite transforms into austenite, there is a preliminary stage where all its ferrite is consumed; but a considerable amount of cementite remains undissolved. This sluggishness in the dissolution of cementite is observed in carbon steel and, more markedly, in certain alloy steels.

Disregarding for the moment the location of the austenite nuclei, on heating slowly to temperature T_1 (fig. 17), somewhat above A_1, or holding at such a temperature, the transformation front passing gradually through pearlite regions will leave behind it austenite with remnants of cementite but no remnants of ferrite. In the still untransformed regions of pearlite, the ferrite will react with cementite and approach its saturation composition for temperature T_1 with respect to cementite α_{c1}, whereas the ferrite at the transformation front will, for a similar reason, approach

Fig. 15 (left)—Acicular growth of austenite in an 0.06C Ni-Cr-Mo steel.

Water quenched after heating at 1450°F ½ hr and tempered ½ hr at 600F. Etched in picral-zephiran chloride reagent. X1000.
Dark etching structure (tempered martensite) was austenite at time of quench.

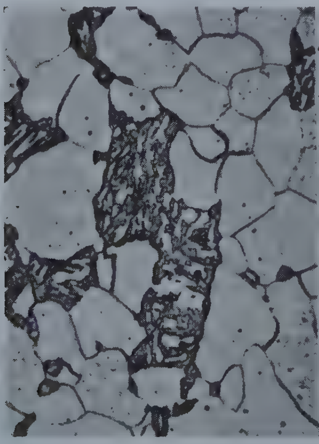


Fig. 16 (right)—Prior structure in the same steel before austenitizing.

As-forged structure tempered at 1300°F. Etched electrolytically in Allten's reagent. X1000.
Dark etching structure represents the areas of martensite or bainite present in the as-forged structure, agglomerated by tempering.

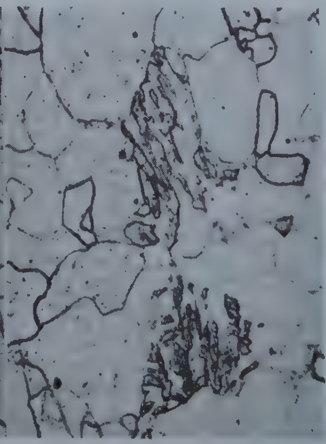
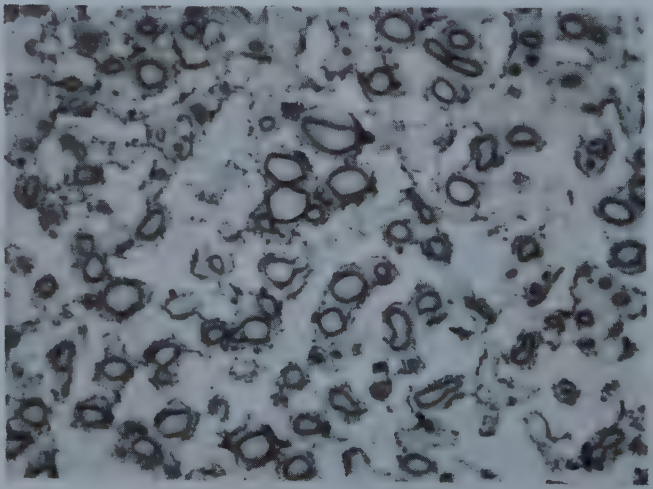


Fig. 18—Symmetrical growth of austenite around spheroidal carbides in a 1.25 pct carbon steel. Area shown is in the heat-affected region of a spot weld. X2000.



the composition α_{a1}. Thus a carbon concentration gradient is set up in the ferritic matrix of pearlite regions, diffusion results; and the carbide of those regions is gradually dissolved in the ferrite, first in the border regions near the advancing austenite, later farther inwards. In this way, the carbon in the cementite of the pearlitic regions will be transported into the austenite, as well as the amount of carbon dissolved in the remaining ferrite in excess of α_{a1}.

This addition of carbon from the ferrite will enable the austenite to grow, its front composition remaining at or near γ_{f1}. Meanwhile, the cementite particles in the austenite will slowly dissolve, in the present case more slowly than the cementite particles in the ferrite. To what extent this sluggishness may be attributed to slow rate of dissolution or slow rate of diffusion in austenite, and to what extent it is effected by alloy elements present, remains an open question.

The author's observation, as demonstrated in figs. 13 and 14, that in hypoeutectoid steels nucleation of austenite may start in the proeutectoid ferrite, is interesting. In this connection it should be borne in mind that at least part of the proeutectoid ferrite generally is precipitated below A_1. This will apply particularly to alloy steels, where precipitation is more sluggish. The composition of such ferrite, as newly formed, would therefore correspond to a temperature T_2 below A_1, and be represented schematically by α_{a2} (fig. 17). On further cooling or on reheating, carbide may be precipitated from this supersaturated ferrite, preferably along prior austenite grain boundaries, or ferrite grain boundaries.* Whether carbide precipitation occurs in the ferrite or not, it is obvious that the conditions for the formation of austenite nuclei on heating are at hand in a ferrite that had once a carbon content exceeding the value α_a for the reheating temperature.

J. R. Vilella and **R. A. Grange**—In common with certain other transformation phenomena, actual observation of the manner of austenite growth in steels heated above their Ac_1 temperature provides numerous exceptions to the classical, and often idealized, conception described in the literature. In his excellent paper, Mr. Nehrenberg has clearly demonstrated that prior structure markedly influences the growth pattern of austenite; since this appears not to have been recognized previously, at least in published literature, his contribution is indeed valuable.

One of the present writers prepared the specimens used as illustrations by Bain[3] and, consequently, is able to provide experimental details not available to Mr. Nehrenberg when he attempted to duplicate these structures. Both steels in which austenite formation was illustrated by Bain were chosen for this purpose

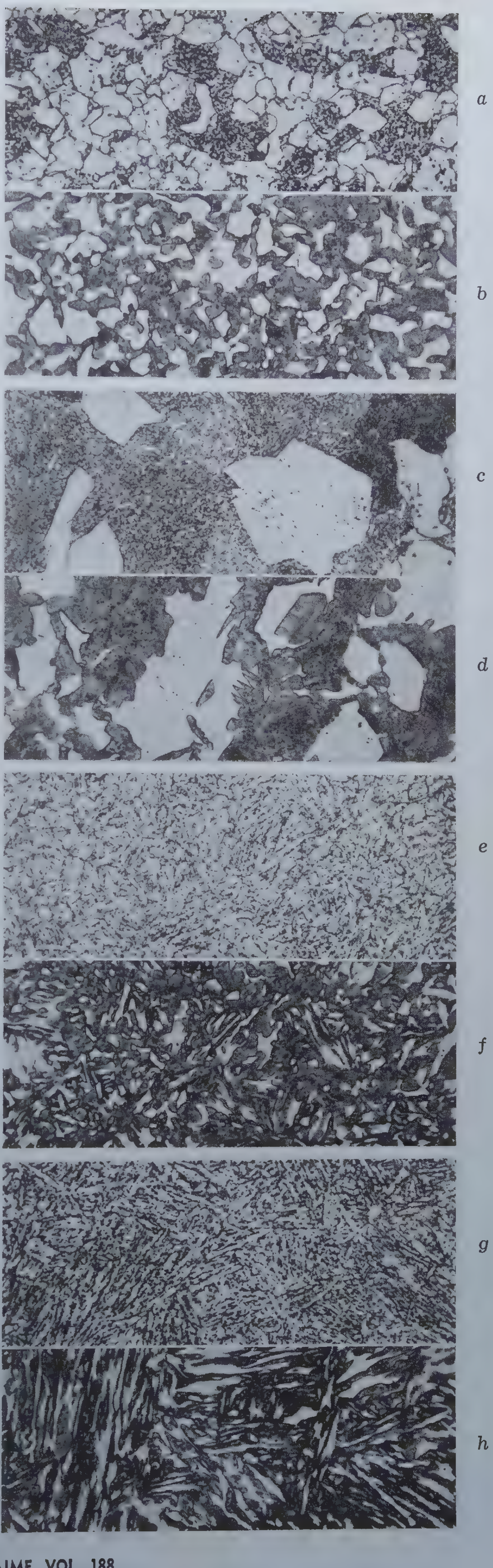


Fig. 19—Effect of prior structure and grain size upon the growth of austenite in an 8630 steel. X1000.

(*a*) Austenitized at 1600°F, isothermally transformed at 1200°F to ferrite and pearlite, and tempered for 16 hr at 1300°F (below Ac_1).
(*b*) Specimen (*a*) reheated to 1385°F (above Ac_1) for 1 hr and brine quenched.
(*c*) Same as (*a*) except austenitized at 2000°F instead of at 1600°F.
(*d*) Specimen (*c*) reheated to 1385°F for 1 hr and brine quenched.
(*e*) Austenitized at 1600°F, brine quenched to martensite, and tempered for 16 hr at 1300°F.
(*f*) Specimen (*e*) reheated to 1385°F for 1 hr and brine quenched.
(*g*) Same as (*e*) except austenitized at 2000°F instead of at 1600°F.
(*h*) Specimen (*g*) reheated to 1385°F for 1 hr and brine quenched.

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* Such evidence will be presented in a paper soon to be published.

because they contained unusually large carbides. The high-carbon steel was produced by carburizing a sample of commercially pure, electrolytic iron. The prior structure, developed by slow cooling from the carburizing temperature, consisted of massive carbides, with occasional carbide lamellae, and ferrite. The low-carbon steel was taken from an oil refinery tube which had been in service at a temperature of 1000° to 1200°F for several years.

In view of the unusual nature of these two steels, it is understandable why Mr. Nehrenberg was unable to develop, by conventional heat treatment of commercial steel samples, carbides comparable in size to those in Bain's illustrations. Mr. Nehrenberg also failed to find a steel in which the majority of the growing volumes of austenite enveloped large carbides; this led him to conclude that "the idealized symmetrical growth of austenite around coarse, spheroidized carbides occurs rarely in commercial steels austenitized in the conventional manner by continuous heating." The two steels in which austenite formation was discussed by Bain were not ordinary commercial steels which had been given a conventional heat treatment and hence, observations based on them do not necessarily conflict with Mr. Nehrenberg's conclusion. However, symmetrical growth of austenite around large carbide particles may not be as rare as Mr. Nehrenberg infers. An excellent example of symmetrical growth was recently encountered in the heat-affected zone of a spot-welded sheet of commercial steel containing 1.25 pct C; fig. 18 is a micrograph illustrating the mode of austenite growth in this specimen. The prior structure was spheroidite. We were not informed of the details of heat treatment, but probably the steel, initially pearlitic, was alternately annealed and cold rolled to reduce it to thin sheet with a microstructure of spheroidized carbides in ferrite. In fig. 18, the boundary between martensite (austenite before cooling to room temperature) and ferrite contains a fringe of dark-etching dots which are believed to be pearlite which transformed, in a manner analogous to formation of the pearlite illustrated by Mr. Nehrenberg in his fig. 6, from austenite during cooling.

Incidental to measurement of Ae_1 and Ae_3 temperatures of commercial steels, we have observed the formation of austenite in many compositions and for a variety of prior structures. In agreement with Mr. Nehrenberg's observations, our experience indicates that the pattern of growth of austenite is noticeably acicular when the prior structure was martensite or bainite, as contrasted to more or less equiaxed growth when the prior structure was pearlitic; thus, the shape of a growing volume of austenite is, to a considerable extent, inherited from the shape of the prior ferrite grains. Mr. Nehrenberg explains this by assuming

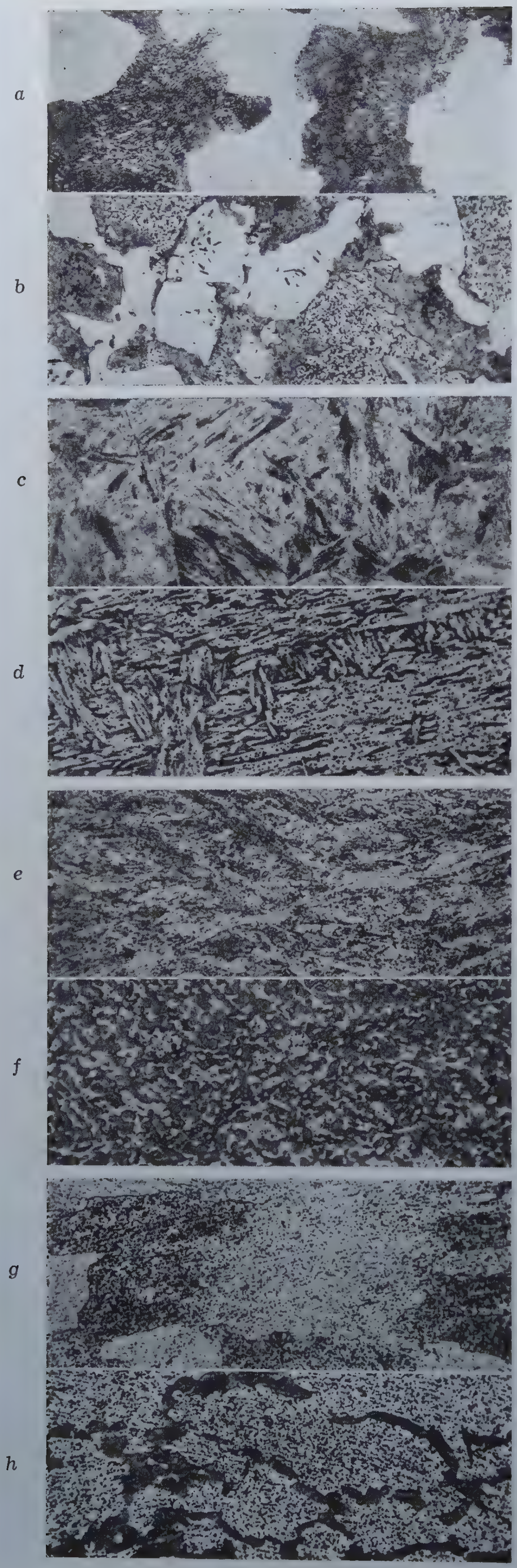

Fig. 20—Four modes of austenite growth in an 8630 steel. X1000.

(*a*) Austenitized at 2000°F and isothermally transformed at 1200°F to ferrite and pearlite.
(b) Specimen (*a*) tempered for 1 hr at 1300°F (below Ac_1), reheated to 1370°F (above Ac_1) for 1 hr and brine quenched.
(c) Austenitized at 2000°F and brine quenched.
(*d*) Specimen (c) tempered for 1 hr at 1300°F, reheated to 1370°F for 1 hr, and brine quenched.
(*e*) Specimen (c) tempered for 1 hr at 1300°F and cold rolled to 50 pct reduction in thickness.
(*f*) Specimen (*e*) reheated to 1370°F for 1 hr and brine quenched.
(*g*) Specimen (*c*) (cold rolled) heated to 1300°F for 1 hr to recrystallize ferrite grains.
(*h*) Specimen (*g*) reheated to 1370°F for 1 hr and brine quenched.

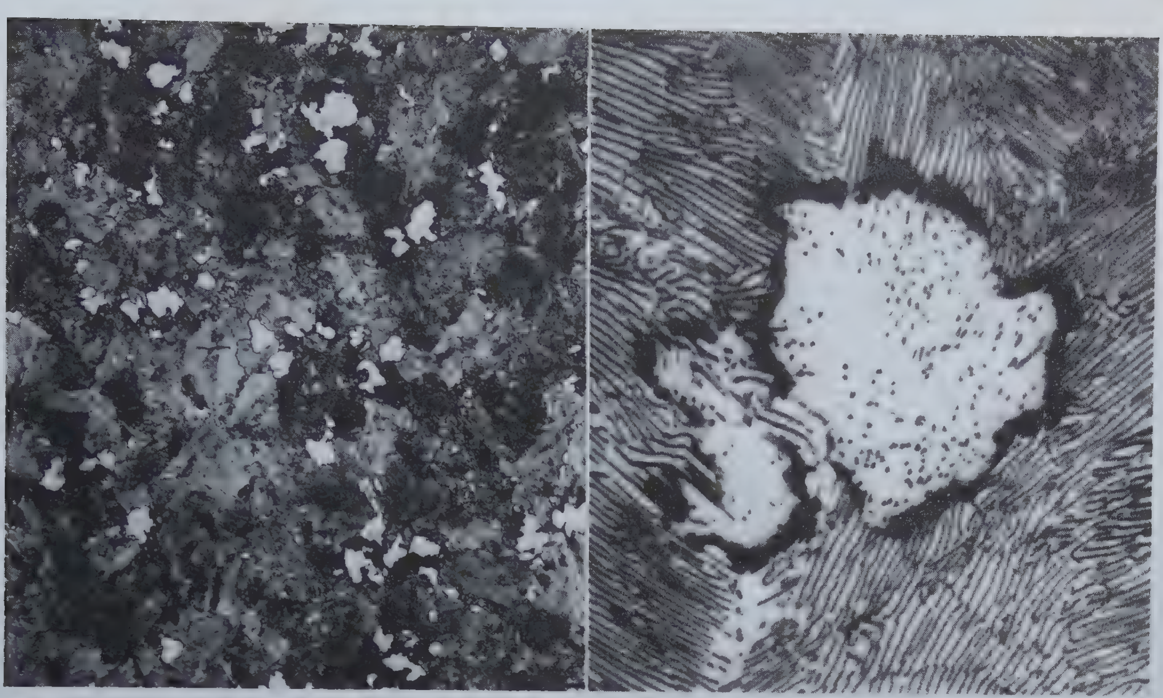

Fig. 21—Formation of austenite in a plain carbon eutectoid steel with a pearlitic prior structure. Specimen held for 8 sec at 1375°F and brine quenched. (*a*) X150, (*b*) X2500.

that, in its early stages of growth, austenite is largely confined in the ferrite grain within which growth started and is reluctant to cross the boundary into an adjacent ferrite grain. Additional evidence supporting this sort of mechanism is afforded by the observation that the average size of growing austenite areas is proportional to the average size of the prior ferrite grains. We have prepared a series of micrographs, shown in fig. 19, to illustrate this, using samples from a commercial heat of 8630 steel. The micrographs are arranged in four pairs in which the prior structure, tempered at 1300°F to emphasize the size and shape of ferrite grains, is the upper member and the structure illustrating the growth of austenite the lower member of each pair; the latter structure was produced by heating at 1385°F (between Ac_1 and Ac_3) for 1 hr and then quenching in brine. Prior structures were pearlitic in *a*, *b*, *c*, and *d* and martensitic in *e*, *f*, *g*, and *h*. Specimens were austenitized at 1600°F or at 2000°F to develop, respectively, small and large austenite grains, which transformed to relatively small and large ferrite grains. Martensitic structures were developed by brine quenching from the austenitizing temperature and pearlitic structures by isothermal transformation of austenite at 1200°F. In the fine-grained pearlitic structure, prior ferrite grains are equiaxed and relatively small, and this shape and size persists in the excess ferrite during austenite formation. In the coarse-grained pearlitic structure, prior ferrite grains are equiaxed but much larger, and the excess ferrite during austenite formation is correspondingly large and equiaxed. Ferrite grains in both fine and coarse-grained martensitic structures (after tempering) are noticeably acicular rather than equiaxed, especially in the latter; after quenching from between Ac_1 and Ac_3, ferrite grains are principally acicular in shape in either case, but, on the average, considerably larger in the coarse-grained sample in accordance with the average size of ferrite grains in the prior structure. Thus, it is apparent that the growth of austenite is related to the size, as well as to the shape, of prior ferrite grains.

Mr. Nehrenberg's work demonstrates that the mechanism of the growth of austenite is more complex than suggested by the classical conception of symmetrical random growth around carbide particles. In this we concur, but believe that he may have somewhat oversimplified the subject. For example, he infers that austenite formed from a martensitic prior structure always assumes, in its early stages of growth, an acicular shape. We would like to cite two exceptions and to illustrate, in fig. 20, four modes of austenite growth in four samples from the same steel given an identical austenitizing treatment, but each having a different structure prior to the final treatment between Ac_1 and Ac_3. The two upper pairs of micrographs in fig. 20 show the mode of austenite growth starting with pearlite (*a* and *b*) and with martensite (*c* and *d*); the prior structure is the upper member of each pair and, in the case of martensite, has been etched in picral plus hydrochloric acid in order to emphasize the acicular appearance of martensite. The third pair (*e* and *f*), in fig. 20, represents an initially martensitic structure, identical to that shown in *c* and *d*, which was tempered at 1300°F for 1 hr and then cold rolled to 50 pct reduction in thickness; although the prior structure was acicular and cold rolling produced elongated ferrite grains, austenite apparently formed principally by equiaxed growth. When the cold-reduced sample was heated to 1300°F (below Ac_1) for 1 hr after cold rolling, the slender, elongated ferrite grains recrystallized to relatively large and only slightly elongated grains (*g* and *h* in fig. 20). In this sample, austenite formed in an unusual network pattern. It is apparent that, despite a martensitic prior structure, austenite growth was by no means acicular in the cold-rolled or the cold-rolled plus annealed samples.

The four so-called modes of austenite growth illustrated in fig. 20 do not necessarily involve four different growth mechanisms, nor do they necessarily comprise all the variations possible in this particular steel, but they do indicate that the mode of austenite growth may vary widely and is probably controlled by more factors than are at present recognized. Incidentally, fig. 20

reveals appreciably more austenite in the cold-reduced specimen than in the other three. This cannot be attributed to difference in the heat treatment during which austenite formed, since all four specimens were heat treated in the same furnace simultaneously; apparently, the cold work accelerated the phase change, which resulted in a closer approach to the equilibrium structure, as might be expected.

Finally, we note that the paper contains no illustration of austenite forming from a pearlitic structure which contains no excess ferrite and in which carbides have not noticeably coalesced either before or during austenite formation. Since, in practice, austenite often forms from such a structure, we show in fig. 21 a micrograph at low and at high magnification of austenite forming under these conditions. In this case, there is no excess ferrite and, hence, no ferrite grain boundaries to restrict random growth of austenite.

O. Zmeskal—Mr. Nehrenberg is to be congratulated on this very excellent paper. It is a penetrating analysis from direct metallographic evidence. He has clearly defined the relationship that exists between the ferrite distribution and the distribution of the austenite that grows from it during the range of two phase equilibrium.

Although the shape of the homogeneous austenite grains could not be determined from the figures, it is probably true that their shape is independent of its acicular or blocky nature while growing in the two-phase field.

A. E. Nehrenberg (author's reply)—The author would like to take advantage of this opportunity to express to the discussers his sincere thanks for their valuable contributions, they are welcome additions to the paper.

It is clear that a great deal of effort was expended by Messrs. Vilella and Grange in the preparation of their comprehensive discussion, and for this the author is most grateful. Since they are well known for their contributions to the literature on transformations in steels, it is pleasant to know that their independent observations confirm the relationships between prior structure and the growth pattern of austenite described in the paper. The metallographic evidence offered in fig. 19 in support of the mechanism suggested in the paper to account for these relationships adds a great deal to the value of the paper.

The fact that Messrs. Vilella and Grange did not observe an acicular growth of austenite in cold-worked tempered martensite does not contradict the concept that the austenite tends initially to assume the size and shape of the ferritic matrix grains. Although the cold-worked grains were initially elongated, during heating to the austenitizing temperature, recrystallization would undoubtedly occur. Thus, the austenite would be forming in an equiaxed structure. This would account for the equiaxed growth of austenite indicated by fig. 20*f*.

Fig. 20*g* indicates that the 1 hr temper at 1300°F not only recrystallized the cold-worked tempered martensite but resulted in considerable grain growth as well. Fig. 20*h* suggests that in such a prior structure the new austenite at first grows preferentially within the grain boundaries of the prior structure. At a somewhat higher austenitizing temperature, it would probably be found that the austenite would assume the size and shape of the coarse equiaxed grains in the prior structure.

Fig. 18, contributed by Messrs. Vilella and Grange, is an interesting example of the symmetrical growth of austenite around large carbide particles. Evidently, when very rapid rates of heating are employed, as in electric welding processes, or perhaps in high-frequency induction heating, the manner in which austenite grows may be less dependent upon the prior grain structure than it is for slower rates of heating.

In connection with fig. 21 of Messrs. Vilella and Grange's discussion, whether there is excess ferrite or not, new austenite tends to assume the size and shape of the matrix grains. Baeyertz[9] found that "austenite grains do not readily grow across the ferrite grain boundaries which separate the pearlite colonies, so that, in the absence of coarsening, the austenite grain size at the end of the transformation is equal to, or less than that of the prior pearlite colony size." The present author has made similar observations.

In Professor Hultgren's discussion an explanation is offered for the fact that the carbides disappear in the ferrite areas before they disappear in the austenite areas in partially austenitized hypoeutectoid steels. Under equilibrium conditions, compositions at various interfaces would be those indicated by Professor Hultgren, but it may be that the rate of heating employed in the investigation described in the paper, that is 60°F per hr, was not slow enough to permit the equilibrium compositions to be attained. Nevertheless, carbon concentration gradients of some magnitude must exist in both the ferrite and austenite to set the stage for the diffusion of carbon to the boundary regions of the growing austenite. As Professor Hultgren has pointed out, the carbides dissolve simultaneously but at different rates in both the austenite and ferrite, and carbon diffuses through both phases to the austenite boundary regions of low-carbon content. The fact that the carbides disappear first in the ferrite can be attributed to a higher diffusion rate in ferrite than in austenite at the same temperature. In this connection Stanley[36] has found the diffusion of carbon to be over 100 times as fast in ferrite as in austenite at the A_1 temperature.

In the concluding part of his discussion Professor Hultgren points out that there is a tendency for carbides to precipitate during cooling to room temperature in proeutectoid ferrite formed just below the A_1 temperature, and that conditions therefore exist in the ferrite which are favorable for the nucleation of austenite during subsequent heating. The exact sites at which nucleation of austenite occurred in the proeutectoid ferrite areas could not be observed, but there were precipitated carbides present. It is reasonable to conclude that nucleation did occur at these carbide-ferrite interfaces.

The micrographs presented by Mr. Schmucker which show evidence of both acicular and equiaxed growth of austenite in a 0.06 C Ni-Cr-Mo steel are appreciated. As the discusser mentioned, the austenite appears to be growing in an equiaxed manner in the equiaxed proeutectoid ferrite, whereas in the tempered martensite or tempered bainite in the same specimen the growth is acicular. This observation is in accordance with the effect of prior structure discussed in the paper and serves to extend the relationships described to commercial steels of very low-carbon contents.

As Professor Zmeskal points out in his discussion, the austenite grains, though they may be initially acicular, finally become equiaxed when the heating for austenitizing is continued to temperatures above the two-phase region. The mechanism by which this transition from acicular grains to equiaxed grains occurs has not been made clear by the work which has been done to date.

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[36] James K. Stanley: The Diffusion and Solubility of Carbon in Alpha Iron. *Trans.* AIME, 185, 752-761; *Journal of Metals* (Oct. 1949) TP 2679E.

Discussion — Extractive Metallurgy Division*

New York Meeting, February 1950

The Electrical Resistivity of Titanium Slags (paper by J. L. Wyatt. *Journal of Metals,* Aug. 1950, TP 2887D) 1382

The Relationship Between Electrical Conductivity and Composition of Molten Lead Silicate Slags (paper by A. K. Schellinger and R. P. Olsen. *Journal of Metals,* Dec. 1949, TP 2728D) 1383

Thermodynamic Relationships in Chlorine Metallurgy (paper by H. H. Kellogg. *Journal of Metals,* June 1950, TP 2869D) 1387

Fundamental and Practical Factors in Ammonia Leaching of Nickel and Cobalt Ores (paper by M. H. Caron. *Journal of Metals,* Jan. 1950, TP 2739D) 1387

Separation of Nickel and Cobalt (paper by M. H. Caron. *Journal of Metals,* Jan. 1950, TP 2740D) 1387

St. Louis Meeting, February 1951

The Graphical Representation of Metallurgical Equilibria (paper by C. J. Osborn. *Journal of Metals,* March 1950, TP 2720CDE) 1388

Columbus Meeting, September 1949

Titanium Investigations: Research and Development Work on the Preparation of Titanium Chloride and Oxide from Titanium Mattes (paper by R. G. Knickerbocker, C. H. Gorski, H. Kenworthy, and A. G. Starliper. *Journal of Metals,* Nov. 1949, TP 2706D) 1388

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* TP 2958D.

Electrical Conductivity of Titanium Slags

by J. L. Wyatt

DISCUSSION

J. W. Tomlinson—It seems probable that the author's conclusion, that the conductivity of the slags decreases with increasing content of FeO, is erroneous due to the method of plotting the data. Thus, the results of other workers[2, 3, 13, 14] show that the conductivity of molten oxide slags increase with increasing temperature, indicating that the trend of the curve shown by the authors is due to the fact that the data for the slags containing relatively small amounts of FeO are at higher temperatures than those for the slags containing relatively large amounts of this oxide. In this connection the work of Wejnarth[2] may be mentioned in which in an investigation of a series of iron silicate slags, the conductivity was found to increase with increasing content of FeO; the fact that the author's slags contained TiO_2 probably does not affect the issue since it has been shown[15, 16] that, at least as far as conductivity is concerned, this oxide behaves essentially the same as silica and that mixtures of the oxide with silica have a very low conductivity of the order of 10^{-4} mhos at 1750°C.

In connection with the experimental technique it may be noted that bubbles of carbon monoxide would probably be produced at the surface of the graphite electrodes in contact with the melts thus rendering the accuracy of the measurements somewhat open to question.

J. L. Wyatt (author's reply)—Dr. Tomlinson makes reference to works by Martin and Derge, which indicate that slag systems containing no TiO_2 are characterized by an increase in conductivity with an increase in temperature. Further, I have cited his examples, which indicate a drastic increase with small temperature change.

The results of Dr. Derge's work have no bearing whatsoever on the results of this paper, since the slags under study here contained up to 70 pct TiO_2. One cannot generalize on slag systems as a whole on the basis of any one family, for there are definite compounds of ionic nature formed in each system, and the ionic mobilization of these is something that cannot be determined without actual experimentation.

Dr. Tomlinson makes reference to an unpublished work which, he claims, shows that titanium dioxide behaves the same as silica in regard to conductivity. Since I have not had an opportunity to see the paper I cannot make any comments, but unless the same slag system was studied there can be no specific comparison of results.

If the decrease in conductivity of the slag was due entirely to temperature phenomena, as Dr. Tomlinson indicates, then one is without an explanation of the values shown in the paper for slags containing from 10 to 20 pct FeO. I cannot agree that the deviation in findings was appreciably related to temperature change; further, I believe this point was completely covered in the paper.

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J. W. TOMLINSON, Massachusetts Institute of Technology, Cambridge, Mass.

The Relationship Between Electrical Conductivity and Composition of Molten Lead Silicate Slags

by A. K. Schellinger and R. P. Olsen

DISCUSSION,

G. Derge—This is an interesting example of the recent recognition that measurement of electrical properties of molten slags provides a direct method for determining slag properties at temperature. Although the authors have properly confined themselves to a simple system, there is certainly no reason to believe that suitable calibration of the influence of other components should not result in a rapid, direct method of slag control.

The discontinuity in the unit conductivity vs. composition curve in fig. 2 corresponds to the possible transition from a trisilicate to a disilicate unit in the slag structure, as indicated in the analogous $FeO\text{-}SiO_2$ system by slag-metal distribution studies.[6] I wonder if the authors have any additional evidence at intermediate compositions to indicate how abrupt this change is.

J. O. Mack—The authors have presented an interesting paper on a proposed method for predicting the relative proportions of PbO and SiO_2 in a binary molten slag from its specific conductivity at different temperatures. If this method can be adapted to production testing, considerable savings in time and money in the testing of slags may be realized.

The similarity between the energy curves for electrical conductivity and viscosity is interesting. Many experimenters have concluded that there may be some sort of relationship between electrical conductivity and viscosity of molten silicates;[3, 7–18] but the relation may not be as simple as the energy equations imply:

$$\gamma = A_k\, e^{Q_k}/RT$$
$$\eta = A_n\, e^{Q_n}/RT$$

Where: γ = conductivity
η = viscosity
Q_k and Q_n = energies of activation
A_k and A_n = constants.

For instance, viscosity and electrical conductivity may exhibit varying degrees of deviation from the energy equations.[3–4, 13, 17–19] Taylor, in particular, cautions that the linear logarithmic relations should not be extended over large temperature ranges.[20] On the other hand, these two properties are different entities, and the results of this paper and the proposed method of slag analysis are not necessarily dependent on a direct relationship between them.

In the presentation of their paper, Mr. Schellinger ably discussed the precautions they took in order to insure a constant depth of electrodes in the molten slags. Inasmuch as this important information was omitted from the published paper, I would like to suggest that it be included in the authors' reply to the discussion. For instance, if such precautions had not been taken, the change in density with chemical composition could affect the depth of the electrodes, particularly when samples of constant weight are selected for testing.[3, 13] A variation in depth of the electrodes from slag to slag would thus affect the transition from the authors' fig. 1 to fig. 2.

A survey of the literature on this interesting subject reveals three other precautions that should be considered in performing this type of study:

1. Herty et al.[21] state that bubbles in the melt will affect its viscosity; they should also affect its conductivity. Martin and Derge and Bockris and coworkers realized this source of error and took appropriate precautions in their investigations.

2. In a study of the relation between electrical conductivity and temperature in molten silicates, White

G. DERGE, Metals Research Lab., Carnegie Institute of Technology, Pittsburgh, Pa.; J. O. MACK, Research Lab., Carnegie Illinois Steel Corp., Pittsburgh, Pa.; J. W. TOMLINSON, Massachusetts Institute of Technology, Cambridge, Mass.

Table I. Liquidus Temperatures of Slags

Slag No.	Mol Ratio, SiO_2/PbO	SiO_2 Wt Pct	Liquidus Temp, °C	Liquidus $1/T_A$x10^5	No. of Points below Liquidus
15	0.412	10.0	735	99.2	1
16	0.500	11.8	743	98.4	2
17	0.650	14.7	730	99.7	1*
19	1.000	21.2	764	96.5	3
20	1.125	27.3	745	98.2	1
21	1.500	29.7	735	99.2	0
22	1.600	20.1	755	97.3	1

* Very close to the liquidus

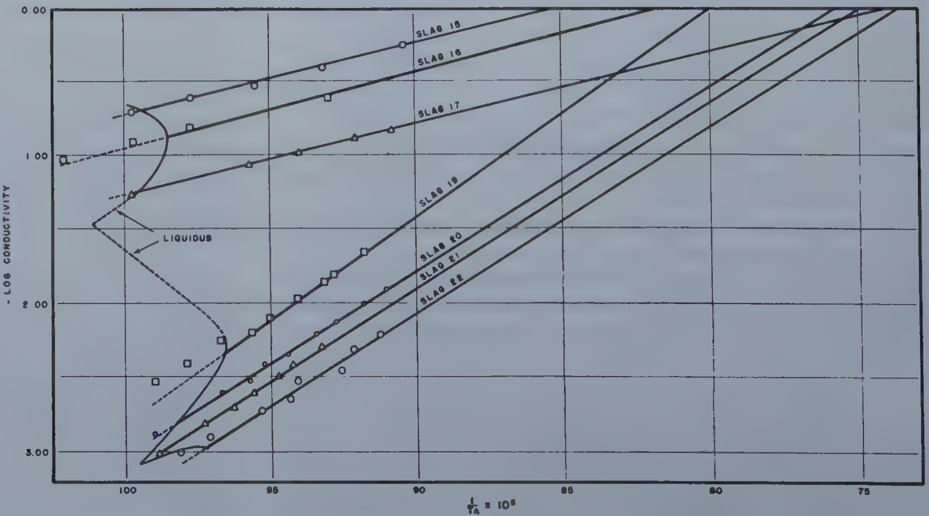

Fig. 3—Data of authors' replotted. Liquidus curve is shown. All points below liquidus were ignored in drawing the lines.

Note the deviations of the points below liquidus of Slags 19 and 22.

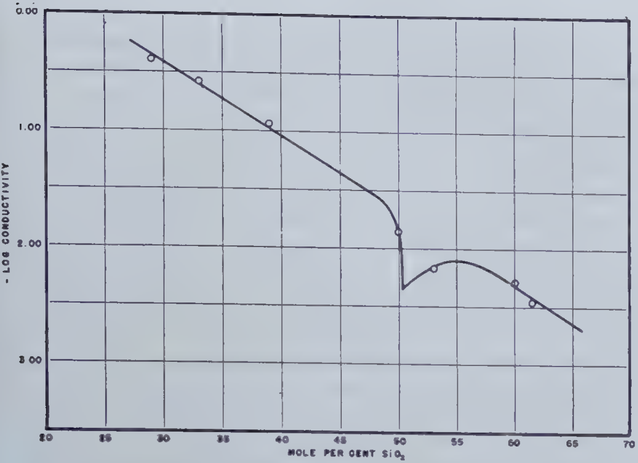

Fig. 4—Effect of composition on electrical conductivity of $PbO\text{-}SiO_2$ slags at 800°C. (From data of authors.)

and Ford[22] held the slag at the desired temperature for a suitable length of time to permit a better approximation of equilibrium conditions. In so doing they detected a difference between their data and those of other investigators particularly near the melting points of the slags. Time at the testing temperature, therefore, apparently has an effect on the electrical conductivity of molten slags. This observation is in agreement with data on the time required for molten slags to reach an equilibrium cell-electromotive force,[23] for example, 44 min at 1450°C for a slag containing 15 pct Al_2O_3, 30 pct CaO, and 55 pct SiO_2 by weight.

3. Incipient crystallization at temperatures below the liquidus of molten silicates can affect the measurement of viscosity[24] and should, therefore, also affect the measurement of conductivity. As long as the molten slag remains vitreous below the liquidus, its conductivity should be continuous with that above the liquidus. If the molten slag is held at a temperature below the liquidus long enough to approach equilibrium conductivity, incipient crystallization may well occur, giving data that are not consistent with those of the completely molten slag.

It is interesting to note that nine of the points shown by the authors were obtained at temperatures below the liquidus of the $PbO\text{-}SiO_2$ system; one of these points, however, was very close to the liquidus. According to the phase diagram they used,[5] the temperatures for initial solidification of each of their slags is listed in table I.

In some of the slags these points are apparently within the experimental error of the higher temperature; this probably means that the slags were sufficiently vitreous at the time of their measurement to preclude any deviation from a continuous relationship. Their data have been replotted in fig. 3, in which the liquidus curve is also indicated. New lines are drawn only through those points that are above the liquidus curve. The deviation of the points below the liquidus of Slags 19 and 22 is apparent.

Only two points were used to draw the line for Slag 16; therefore, the line was drawn parallel to that of Slag 15. Such a parallelism may not be correct, particularly since Slag 16 corresponds to the compound $2PbO \cdot SiO_2$. On the other hand, there are not enough data to do otherwise.

Fig. 4 shows the effect of chemical composition on the conductivity at 800°C as obtained from the data of the authors. The three points on the left and the two on the right form a straight line. The two points near the center of the graph, however, are appreciably lower than this line. A downward cusp has been drawn into the curve at the composition of $PbO \cdot SiO_2$, at which there is a maximum in the liquidus curve (746°C). Several investigators[21, 25-27] have reported this type of minimum in viscosity curves for stoichiometric compounds in other silicate systems; others[20, 28] have predicted such minima. (However, Lillie[29] and Endel et al.[24] did not find such minima.) To the best of my knowledge, however, this type of minimum has not been reported heretofore for electrical conductivity-chemical composition curves for molten slags.

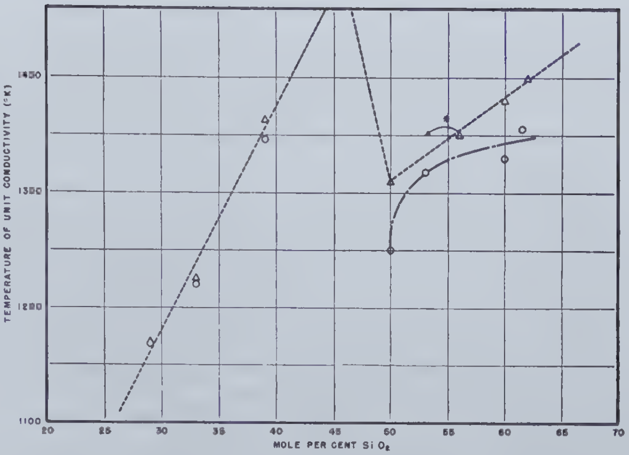

Fig. 5—Original curve from fig. 2 of the authors showing one point that was misplotted and revised points from the lines of fig. 3.

*** Point miscalculated by Schellinger and Olsen. Δ—Schellinger and Olsen. O—Points recalculated from revisions in fig. 3.**

The work of Preston[25] is particularly noteworthy. In his early work on the viscosity of the $Na_2O\text{-}SiO_2$ system, he obtained only a few points, which were slightly scattered and through which he drew a straight line. Later, when he obtained many more points, he observed two downward cusps, one at $Na_2O \cdot SiO_2$ and one at $Na_2O \cdot 3SiO_2$, the latter being less pronounced.

The authors' curve in fig. 2, is reproduced as a part of fig. 5; one point on their curve seems to be misplotted, the correct position being indicated by an arrow. The curve resulting from the new lines drawn in fig. 3 is also included. It appears that the part of the curve on the high-silica side of the diagram may be parabolic instead of linear.

The physical significance of plotting the temperature (K) of unit conductivity against mol pct SiO_2 is not at first apparent. An examination of the energy equation, however, shows that this temperature is a function of Q_k and A_k:

$$\begin{aligned} \log \gamma &= \log A_k + Q_k/RT \\ \text{At } \log \gamma &= 0, -\log A_k = Q_k/RT_1 \\ \text{and } T_1 &= -Q_k/R \log A_k \end{aligned}$$

The effect of composition on Q_k is shown in fig. 6. There is a discontinuity near the center of the graph.

The effect of composition on A_k is shown in fig. 7. The discontinuity is more pronounced in this curve.

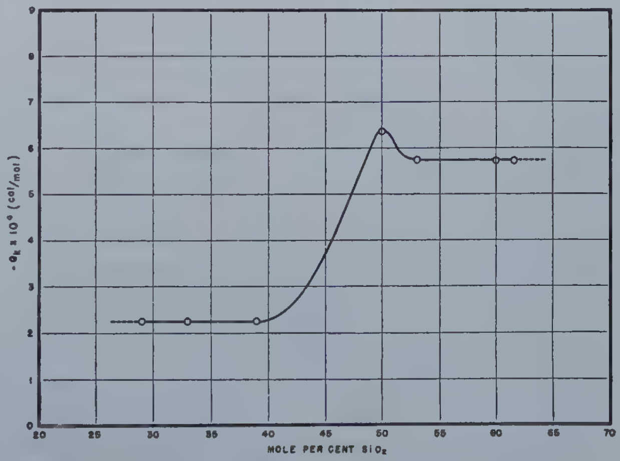

Fig. 6—Effect of composition of $PbO\text{-}SiO_2$ slags on $-Q_k$.

These discontinuities occur at the same composition as that noted by the authors in fig. 2. I would like to suggest that additional data in the range of compositions 40 to 50 mol pct SiO_2 would be helpful in understanding the results obtained in this investigation.

In conclusion I would like to suggest to the authors that experimental data in the form of those in fig. 4 might simplify their problem of relating electrical conductivity to chemical composition. By using this relationship, a conductivity measurement at only one temperature is required. Also, in fig. 3 there is a region in which the test results will indicate up to three widely differing chemical compositions; whereas, in fig. 4, such regions, if really present, are confined to a narrower range of compositions.

Again, I would like to congratulate the authors on their undertaking of this difficult, but very interesting investigation.

J. W. Tomlinson—This work is of great interest and the authors are to be complimented on their approach to a difficult problem.

With reference to the experimental technique, I would like to ask the authors whether they observed any attack of the crucible or the thermocouple and electrodes, and also whether they observed any volatilization of lead oxide from the slags containing high percentages of this constituent; an analysis of the melts before and after the experiments would be of interest in this respect.

The authors assume that ionic conduction in liquids is a function of viscosity and state that the straight line relation they observe between log conductivity and $1/T$ is good evidence of the correctness of the assumption. To avoid confusion it is necessary to clarify this point. The Shepard relation quoted, is a logarithmic form of an empirical expression suggested by Rasch and Hinrichsen in 1908 and Arrhenius in 1916 to relate the variation of conductivity to temperature. For molten salts, expressions have been derived from first principles expressing these two properties, using both kinetic statistical and transition state theory.[30, 31] These treatments show that the empirical expressions cited above are approximations to more exact formulas and hold over limited ranges of temperature. While for most liquids conductivity increases and viscosity decreases with increasing temperature, and while in a binary silicate system it is usual to find that conductivity increases and viscosity decreases with increasing content of the metal oxide, these properties do not show any consistent variation with the type of metal ion. This may easily be seen by reference to molten salts and in particular the halides of the alkaline earth and alkali metals which have been investigated in some detail.

In all cases the energy of activation for viscosity is greater than the energy of activation for conductivity by a factor of the order of 2-6, indicating that the two processes involve different energy barriers. For molten silicates the factor is also of the order of 2-6 and it is now generally acknowledged that the conduction is due to the small metal cations and the viscosity to the silicate groups or anions.[13, 32-35]

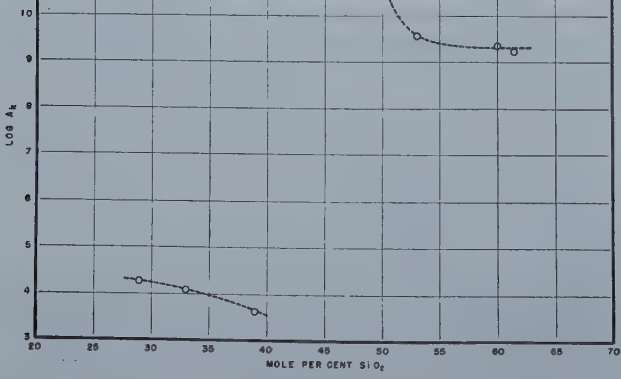

Fig. 7—Effect of composition of PbO-SiO_2 slags on A_k.

The range of temperature for which the lines are shown in fig. 1, extends below the liquidus temperature in all cases except one and measurements in this region are therefore not characteristic of the liquid corresponding to the composition quoted but of a liquid the composition of which depends on temperature. It would be interesting to know if the authors measured any conductivities through the solidification point as a sudden fall in conductivity might be expected at this point.

The inflection point shown in fig. 2 at the composition corresponding to slag 17 is interesting from a theoretical standpoint though it is difficult to do more than speculate, as the point depends on one result only, unless the authors have restricted the data for the sake of clarity; and it is possible to draw a perfectly satisfactory straight line through the other points. Also, the fact that the data fall into two groups may be due to the fact that no results were obtained for compositions between slags 17 and 19. A sudden change in structure would not be expected at this or any other composition on the random network theory of silicate melts which postulates a continuous change in the size of the silicate groups and a corresponding change in the number of conducting cations and the energy of activation for conduction; these conclusions are well supported by experimental data.[13, 32-35]

With reference to the prediction of the composition of a slag from conductivity and temperature measurements, it seems probable that small amounts of impurities of the alkaline earth type would not affect the results substantially. Alkali metals or iron and manganese however, would probably affect the results due to their higher ionic weight conductivity.[13, 32-35]

A. K. Schellinger and **R. P. Olsen** (authors' reply)—We find it gratifying that the results of our modest research have aroused the satisfying discussion which precedes this reply, especially from outstanding workers in the field of molten silicate solutions. We wish to thank these men for their stimulating and thoughtful discussion of our paper and work.

Dr. Derge's suggestion that the discontinuity in the unit conductivity vs. composition curve (fig. 2) may correspond to a transition from a trisilicate to a disilicate unit in the slag structure seems to be a valid one. We must confess, however, that our data is far too scanty to give much evidence as to the abruptness of the transition. The reason for this paucity of data is that we were primarily interested in only sufficient measurements to establish straight-line relationships for the PbO-SiO_2 system in order to predict slag composition from electrical conductivity. We did not have an opportunity at a later date to pursue structural studies such as are illustrated by Dr. Derge's excellent work in this field. Such studies should be made on this simple binary system.

The painstaking and complete discussion of our paper offered by the Carnegie-Illinois Steel Co. Research Laboratory is greatly appreciated. Mr. Mack points out the similarity between the energy curves for the "different entities" electrical conductivity and viscosity. In our paper we point out the almost exact similarity between an empirical equation derived by Shepard, for the viscosity of a pure liquid ($\log \text{viscosity} = A/T + B$) and the equation for electrical conductivity derived from our plotted points ($\log \text{conductivity} = —A/T —B$). We derived the latter equation from the former. While this is certainly not proof of the identity of electrical conductivity and viscosity, it seems to us that the interdependence of the two is so marked that one would be almost justified in claiming electrical conductivity as merely another manifestation of viscosity.

Mr. Mack's second point, having to do with the depth of the electrodes in the slag whose conductivity was being measured, is well taken. In our work a special assembly consisting of two platinum wire electrodes, each covered with a single-hole insulator, except for several millimeters of the wire tip, plus a thermocouple tube, was hung into a 10-g assay crucible to the same depth in each case. The crucible was always filled up to the same mark with the slag to be measured. Calibration of the assembly was made in the same crucible by filling it with standard KCl solutions to the given mark. No variation in depth was possible except by creep of the slag (wetting) up the electrode insulators; this did not occur to any visible degree. In any case, the area of electrode exposed to the slag was exactly the same in all measurements.

With regard to point one of the discussion, we can only say that we did not observe any bubbles in our slags, which were held in the liquid state for a considerable time prior to measurement of their electrical conductivity. This long holding time should also have allowed equilibrium conditions to obtain, another point which Mr. Mack brings to our attention.

In replotting our data several readers found that some of our conductivity points were below the liquidus temperatures for the $PbO-SiO_2$ system and therefore in a two-phase region. We must confess that this was done inadvertently, although it is not too serious in that the straight-line relationships are not visibly affected. We did, however, note that the parallelism of our negative log conductivity vs. $1/T$ lines was not perfect, even though sufficiently marked to allow equations to be written and the relationship between the conductivity and composition to be derived.

The isothermal (800°C) plot of negative log conductivity vs. mol pct SiO_2, given in fig. 4 was also considered by the authors, but the existence of the cusp at 50 pct SiO_2 was not recognized and the temptation was strong to throw out the two deviating points in order to continue the straight line. This would give but one equation for the relationship between conductivity and composition and be quite convenient although inaccurate. The plot of the temperature-of-unit-conductivity vs. mol pct SiO_2 was conceived as a device for obtaining unambiguous straight lines with all the points included. The misplot found by the discusser does not seem to be serious enough to change our straight line, inasmuch as our experimental error was of a greater order of magnitude than that of the work of the structural studies of slag systems. The authors, although apologizing for the error, would still have drawn the line as the best approximation available.

We are prepared to admit that at least twice as many experimental points would be desirable for a more complete and satisfactory study of this slag system from a structural and energetics standpoint. We, however, were pioneering with this system with the objective of discovering straight-line relationships that would be useful as a basis for instrumental control of industrial slags. We are gratified that our data have been found useful in connection with the general picture of the energetics of slag viscosities and electrical conductivities, and wish again to express our appreciation of the painstaking analysis of our data made by Mr. Mack.

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Thermodynamic Relationships in Chlorine Metallurgy

by H. H. Kellogg

DISCUSSION

M. Rey—I wish to point out what appreciation we have in Europe for the pioneer work of the Bureau of Mines and particularly of Kelley in working out the "Contributions to the Data on Theoretical Metallurgy." Every time one of these bulletins comes out, those of us who are interested in metallurgical calculations are eager to get a copy of it.

Kellogg has rendered a service in compiling these data and in making them available in the form of the excellent Ellingham diagrams. The most important of these diagrams is, of course, the one concerning the oxides.

The references at the end of the paper indicate the original publication of Ellingham and another one of Dannatt and Ellingham. A revised diagram for oxides, including a discussion on the accuracy of the various data, has been published by Richardson and Jeffes,[38] of the Chemical Department of the British Iron and Steel Research Association.

Still more recently, diagrams for oxides, sulphides, chlorides, sulphates, and carbonates have been published by Osborn.[39]

The author pointed out that carbon is not a reducing agent for chlorides. Sometimes, a small amount of water vapor, present in the atmosphere of the furnace, may, unknown to the operator, change this situation, because the reaction of water-vapor with carbon produces hydrogen which is a reducer for chlorides. An example of this is the minerals separation segregation process where copper, lead, and silver chlorides are reduced to the metallic form by carbon.

The presence of at least a trace of water vapor in the atmosphere is important for chemical reaction of the process.[40]

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Fundamental and Practical Factors in Ammonia Leaching of Nickel and Cobalt Ores and Separation of Nickel and Cobalt

by M. H. Caron

DISCUSSION

O. C. Ralston—The fact that none of the organizations that have worked on these ammoniacal leaching processes have contributed discussion of Mr. Caron's papers today is a matter of some disappointment. Adaptations, modifications and improvements have been made by several organizations or individuals and to complete the record I want to document a number of them.

The Nicaro Nickel Co. operated a Government owned plant at Nicaro, Oriente, Cuba, during the past war. A report on the project was written for Reconstruction Finance Corp. and is in the document file collected by the Office of Technical Services, Commerce Department and filed with the Library of Congress, where it can be consulted or bibliofilm or photostat copies obtained by asking for copies of PB 97271. Nicaro Nickel Co. has obtained a series of U.S. Patents, my list (probably incomplete) of which bears the following numbers: 2,400,098; 2,400,114; 2,400,115; 2,400,461; 2,400,612; 2,458,902 and 2,473,795.

International Nickel Co. has also studied the problem and U.S. Patent 2,478,942 shows that some of the complications involving occasional low extractions have been unraveled.

Forward, Samis, and Kudryk, of the University of British Columbia, have also published a study of copper-nickel sulphide concentrate.[6]

Others are interested and it is evident that this type of hydrometallurgy is likely to find a happy application in the not-too-far distant future. Caron's two papers practically amount to a summation of his life's work on the important subject of nickeliferous iron ores and the American Institute of Mining and Metallurgical Engineers is fortunate to have been chosen the medium of publication.

M. Rey—The ammonia leaching process has been the subject of certain studies in New Caledonia, but at the present time, the conditions are not very favorable to its adoption.

The process is a combination of a thermal and a hydrometallurgical process. As a result, the first costs and the operative costs are rather high. To counteract this unfavorable situation, it would be necessary to make a very high extraction. But unfortunately, the process is delicate and in spite of all of Caron's valuable work, there are still many unknown factors. It is difficult to obtain regularly a high extraction, exceeding 75 to 80 pct.

It would be interesting to have the opinion of International Nickel on the process and to know what the Dutch are doing in Celèbes.

M. H. Caron (author's reply)—I am quite familiar with the different types of nickel and cobalt ores as found on New Caledonia, and it may be pointed out that the Celèbes ores are quite the same in their properties. Their behavior when treating the ores by the ammonia-leaching process is also alike and in my opinion, there is no reason why a high extraction of the New Caledonian ores could not be obtained if the process is properly applied.

For the sake of completeness I may add that one of my patents has not been discussed in the papers. This patent deals particularly with the treatment of serpentine nickel ores. (Netherlands No. 62693 40a, French No. 965,786 April 21, 1948, and Cuban No. 13,625 Jan. 1950.)

O. C. RALSTON, U. S. Bureau of Mines, Washington, D. C.; M. REY, Ecole Nationale Supérieure des Mines de Paris, Paris, France.

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[6] F. A. Forward, C. S. Samis, and V. Kudryk: *Trans.* Canadian Institute of Mining and Metallurgy. (1948) 151 (Bull. 434) 350-355.

The Graphical Representation of Metallurgical Equilibria

by C. J. Osborn

DISCUSSION

H. H. Kellogg—The free-energy relationships given in this paper are a welcome contribution to the metallurgical literature. The future value of this paper, however, will be largely dependent on the accuracy of curves presented by Dr. Osborn. In this connection there are several serious errors that should be brought to the attention of the reader.

1. Dr. Osborn based his $CaCl_2$ calculations on $\Delta H^\circ 298$ from Bichowsky and Rossini[3] and the entropy value determined by Kelley and Moore.[26] Use of these data result in $\Delta F^\circ 298$ = —179,860 cal per mol of $CaCl_2$. Fig. 3, on the other hand, indicates a value of about —130,000 cal for $CaCl_2$.

2. The use of the data of Bichowsky and Rossini for $\Delta H^\circ 298$ and of Kelley[24] for $S^\circ 298$ of 2NaCl, result in the value $\Delta F^\circ 298$ = —183,820 cal for 2NaCl. Fig. 3, on the other hand, indicates a value of about —134,000 cal for 2NaCl.

The two errors referred to above are very large—too large to be attributed to inconsistencies in the data. The fact that both errors are about 50,000 cal suggests the idea that Dr. Osborn purposely subtracted 50,000 cal from these curves in order to fit them on his diagram and subsequently forgot to indicate the necessary scale correction. In any case, the large error in these curves should be brought to the attention of the reader.

3. Fig. 7 has been plotted incorrectly. The term $(R\ T \ln a)$ is shown to have a value of zero at 0°C for activities greater than unity. Since R and $(\ln a)$ are both finite, positive quantities, and T has the value 273.16° at 0°C, then $(R\ T \ln a)$ must be finite at 0°C. The correct values of $(R\ T \ln a)$ can be obtained from fig. 7 if the abscissa is read as degrees Kelvin instead of degrees Centigrade.

4. Many of the curves deviate by one or two thousand calories from similar calculations that I have made, but these inconsistencies can be attributed to small differences in the basic data used to make the calculations. However, the very important curve for the reaction $2C + O_2 = 2CO$, on fig. 1, deviates widely from modern accepted values in the high temperature region. One of the most reliable of modern sources for thermodynamic data, the "Selected Values of Chemical Thermodynamic Properties," which is published by the U. S. Bureau of Standards, has reported the standard free-energy of CO(g) as a function of temperature (March 31, 1949). A comparison of these values with those read from Dr. Osborn's curve are given in table III.

Table III. Standard Free-Energy of CO(g) as a Function of Temperature

°K	°C	ΔF° for $2C + O_2 = 2CO$	
		"Selected Values"	Osborn, Fig. 1
1,500	1,227	—116,740	—116,500
1,700	1,427	—124,920	—125,000
1,900	1,627	—133,000	—134,000
2,100	1,827	—141,040	—144,500
2,300	2,027	—148,960	—157,000
2,500	2,227	—156,820	—170,000

The error is appreciable above 1600°C and reaches about 13,000 cal at 2227°C. Since this is one of the curves that Dr. Osborn feels is reliable to ± 1000 cal, the reader must accept with caution his reliability estimates.

H. H. KELLOGG, School of Mines, Columbia University, New York, N. Y.

It is unfortunate that these few errors were allowed to mar an otherwise valuable paper.

C. J. Osborn (author's reply)—Professor Kellogg's interest in this paper is greatly appreciated. For the most part, he has correctly interpreted the inconsistencies which he has observed. The curves for $CaCl_2$ and 2NaCl should be labeled "$CaCl_2$ + 50 kcal" and "2NaCl + 50 kcal" respectively, and the abscissa of fig. 7 should obviously read degrees Kelvin. The last point was corrected in the *Journal of Metals* for July.

It is unfortunate that the U. S. Bureau of Standards data sheet for the reaction $2C + O_2 = 2CO$ was not available when this paper was written. In constructing the curve shown in fig. 1, it was necessary to extrapolate the expression for the specific heat of carbon well beyond the limit of its validity. However, in this and in all other cases where extrapolation has been deemed to affect the accuracy of the curve, the nature of the line has been changed in accordance with table I. The high temperature portion of the CO curve was drawn as ±3 kcal, although it now seems that ±10 kcal would have been more correct.

Titanium Investigations: Research and Development Work on the Preparation of Titanium Chloride and Oxide from Titanium Mattes

by R. G. Knickerbocker, C. H. Gorski, H. Kenworthy, and A. G. Starliper

DISCUSSION

In oral discussion at the Columbus midyear meeting, September 26, 1949, these pertinent questions were asked:

Was a satisfactory separation of metal and matte obtained? The matte was quite fluid and in most cases the separation was satisfactory.

Were the mattes chlorinated after aging? The mattes were stored in sealed glass mason jars, and chlorination experiments made after standing for several weeks gave satisfactory results.

Was ferric chloride volatilized? Most of the iron content of the matte was converted to ferric chloride. However, because of the low chlorination temperatures used (150° to 250°C) the major part of the ferric chloride remained with the residue. Undoubtedly, some ferrous chloride was also formed, because of the reducing conditions within the reaction vessel, but no effort was made to separate it from the ferric chloride.

Could the reaction be stopped before making metallic iron? No attempt was ever made to stop the reaction before making metallic iron. Generally, 20 to 60 pct of the iron in the charge was obtained as metallic iron which could be readily separated from the matte. In certain cases, metallic iron was dispersed through the matte in the form of globules, which could be removed by magnetic separation.

Could other sulphides, i.e., calcium sulphide or sodium sulphide be used in place of iron sulphide? No other sulphides were investigated. It was felt that titanates of calcium and sodium would be formed should these sulphides be used to replace the pyrite.

What were the sulphur volatilization losses during matte smelting? In the course of this laboratory investigation, a rather wide variety of variables was introduced from highly oxidizing to reducing conditions and various ratios of pyrite, rutile, and coke. These and other factors all have a definite bearing on the sulphur losses. In general, the higher the sulphur in the charge the higher were the sulphur losses and the percentage of titanium in the matte decreased. With sulphur additions more nearly the theoretical amount, the sulphur losses averaged approximately 10 to 15 pct. With a higher percentage of sulphur on the charges, the losses were in the order of 15 to 30 pct.

The Activity of Sulphur in Liquid Steel; The Influence of Copper

by

Terkel Rosenqvist

and

Earl M. Cox

Steel melts of various sulphur and copper contents were brought in equilibrium with a H_2S-H_2 gas mixture, the composition of which gives a measure of the escaping tendency of sulphur. It was shown that small amounts of copper lowered the sulphur activity, but not sufficiently to affect the desulphurization process.

IN a recent investigation, carried out at the Institute for the Study of Metals, the affinity of sulphur for iron, copper, and manganese was studied over the temperature range 700° to 1300°C.[1] It was found that copper exhibits a rather high affinity for sulphur, especially at higher temperatures; and attention was called to the possibility that copper when present together with sulphur in liquid steel would tend to lower the chemical activity of sulphur and thus interfere with the desulphurization process. It was clear, however, that the data for the equilibrium between pure copper and pure copper sulphide (Cu_2S) could not give any *quantitative* information about the effect of copper when dissolved in liquid steel.

The present work is concerned with the activity of sulphur in the diluted range of the binary iron-sulphur system, and with the influence of small amounts of copper on this sulphur activity. This investigation is in principle based on the same method previously described for the binary metal-sulphur studies;[1, 2] namely, reaction with hydrogen to form hydrogen sulphide. The equilibrium ratio P_{H_2S}/P_{H_2} in the equilibrium gas mixture is, for a given temperature, directly proportional to the sulphur activity. The activity of sulphur in liquid iron has previously been studied by Chipman and Ta Li,[3] White and Skelly,[4] and recently by Sherman, Elvander, and Chipman.[5] Morris and Williams[6] have studied the effect of added silicon, and Kitchener, Bockris and Liberman,[7] and recently Morris and Buehl,[8] the effect of added carbon on the sulphur activity.

In present day steelmaking processes the steel bath contains between 0.01 and 0.1 pct sulphur, and the copper content may be as high as 0.5 pct. The equilibrium gas ratio (H_2S/H_2) would, for such a low-sulphur content, be too low to be measured with the experimental technique we use. It has been shown by previous investigators that the H_2S/H_2 ratio is closely proportional to the sulphur content up to about 1 pct sulphur. The sulphur activity at very low-sulphur content can therefore be calculated by linear interpolation between 0 and 1 pct sulphur. In order to show the general trend with increasing sulphur content, the present work has been carried out to about 3.5 pct sulphur. As the effect of copper was assumed to be more a function of the Cu/S ratio than of the absolute copper content, the runs with copper were made for certain constant values for this ratio.

T. ROSENQVIST is associated with the Institute for the Study of Metals, University of Chicago, Chicago, Ill., and E. M. COX was formerly with the Institute for the Study of Metals.

AIME New York Meeting, February 1950.

TP 2982 C. Discussion (2 copies) may be sent to Transactions *AIME by Jan. 15, 1951. Manuscript received Nov. 23, 1949; revision received March 30, 1950.*

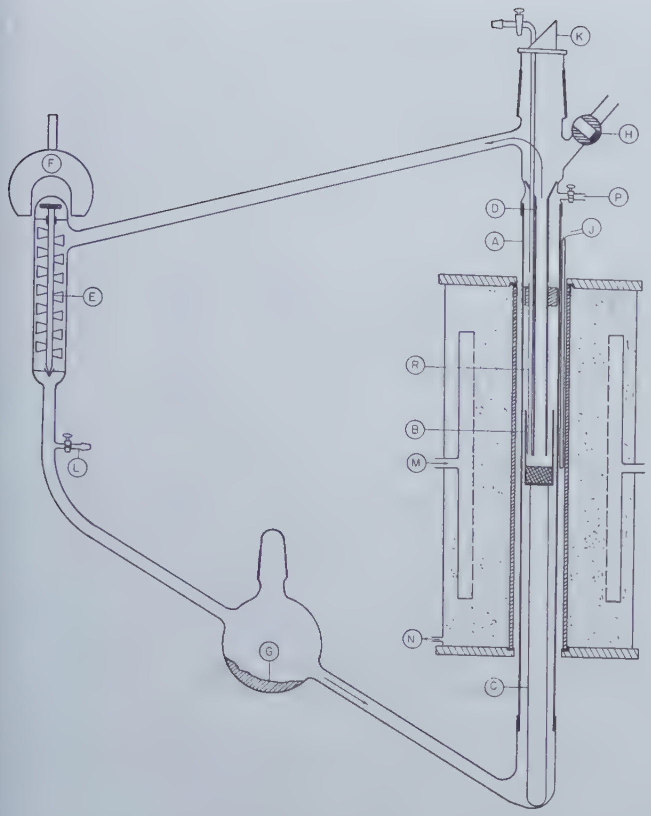

Fig. 1—Apparatus for study of sulphur activity.

A.	Reaction tube
B.	Al_2O_3 crucible with melt
C.	Support
D.	Removable chimney
E.	Glass propeller
F.	Rotating magnet
G.	P_2O_5
H.	Lock for admitting copper
J.	Thermocouple
K.	Prism for sighting optical pyrometer
L.	Stopcock for sampling
M.	Inlet for protecting gas
N.	Outlet for protecting gas
P.	Inlet for pure hydrogen
R.	Capillary for sampling from hot zone

Experimental Procedure

The apparatus (fig. 1) consisted of a gastight system, where the gas mixture, H_2 and H_2S, circulated through the reaction tube *A*, came in contact with the steel melt, and equilibrium between the melt and the gas was established.

The source of heat was a molybdenum-wound resistance furnace with a gastight mullite core. The furnace case was made sufficiently gastight to hold an atmosphere of hydrogen and nitrogen which prevented oxidation of the molybdenum windings.* The inner reaction tube *A* was also of mullite which was the only refractory that proved to be completely gastight at 1500° to 1600°C.

A heavy gauge Pt—Pt-13 pct Rh thermocouple was inserted between the two mullite tubes. It was used to operate the automatic temperature controller, and could also, when corrected for the temperature difference between the thermocouple and the melt, be used to read the temperature of the melt. The thermocouple was checked after each heating period by comparison with a standard thermocouple. It stood up remarkably well, and only minor changes with time were observed for runs at 1550°C. The temperature readings for these runs are regarded as correct to 5°C.

Steel melts of about 100 g were used. They were made up of "Puron" iron to which pure iron sulphide (FeS) was added in varying amounts. Additional amounts of either iron sulphide or electrolytic copper could be added as beads through a "lock" consisting of a large stopcock with one end of the bore closed (fig. 1). This permitted the introduction of material during the run without any gas leaking into or out of the system.

The use of rather large steel batches has the advantage that only a small fraction of the total sulphur (less than 1 pct) has to be transferred across the metal-gas interface to give the equilibrium H_2S concentration in the gas. This means a rapid approach to equilibrium; and it also means that the sulphur content of the melt stays, for all practical purposes, constant during the run, even if the H_2S content of the gas changes considerably. A large steel batch also means that any contamination, such as silicon, transferred through the vapor from the mullite tube, will be diluted to insignificance.

Crucibles made of pure sintered aluminum oxide proved to be very satisfactory. No reaction seemed to take place between the crucible and the atmosphere, or between the crucible and the melt. The steel ingot did not stick to the crucible and could, after cooling (in liquid nitrogen if necessary), be easily removed. One crucible was analyzed after the run and no significant amount of sulphur could be detected.†

The crucible was supported on a tube of sintered aluminum oxide, and the outlet tube for the gas was of the same material. Thus all refractories in the immediate vicinity of the steel bath were free of silica.

A very small amount of water vapor was formed during the runs with aluminum oxide crucibles. This is probably due to a slight reduction of the refractories, and to reduction of any oxides that may be present in the iron. In order to remove this water vapor from the gas some P_2O_5 was placed in the cold part of the system (fig. 1).

After the furnace was brought to the desired temperature, equilibrium between the melt and the gas

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* It was found that, due to the high heat conductivity of hydrogen, the heat losses and consequently the power consumption, were 20 to 30 pct higher when pure hydrogen was used as a protecting atmosphere rather than a mixture of about equal amounts of hydrogen and nitrogen. For some runs a gas mixture with only 20 pct hydrogen was used without harming the winding.

† For a number of runs, crucibles of stabilized zirconium oxide were tried. These crucibles that had proved very useful for melts free of sulphur, were severely attacked by the sulphur in the gas as well as in the melt. As water was observed condensing in the cold part of the system, the reaction was assumed to be of the nature

$$ZrO_2 + 2H_2S = ZrS_2 + 2H_2O$$

It is of interest to notice that in all these runs considerably higher H_2S/H_2 values were found than in runs with alumina crucibles. This phenomenon cannot readily be explained.

was established in less than 4 hr. Gas samples for analysis (about 50 cc) were drawn from the system 4, 5, and 6 hr after the desired temperature, or steel composition, was established.

In a previous paper[2] the factors that tend to change the composition of the gas mixture when passing from the hot to the cold zone of the system have been discussed. These are: (1) thermal diffusion, i.e., inhomogeneity of the gas mixture due to difference in molecular weight of hydrogen and hydrogen sulphide, and (2) formation of additional H_2S by cooling due to a shift of the following equilibrium to the right:

$$H_2 + \tfrac{1}{2}S_2 = H_2S$$

It was originally assumed that the rate of circulation (about 1 cc per sec) was high enough to reduce the thermal diffusion to a minimum, so that the gas mixture in the cold zone was representative of the gas in equilibrium with the melt. In the early part of the work, samples were drawn from the cold part of the system. However, it was found that the circulation of the gas was not rapid enough to overcome thermal diffusion. Samples were then drawn from the hot zone right above the surface of the melt. For this purpose a capillary of pure aluminum oxide was inserted into the furnace (*R*, fig. 1). The gas *inside* the capillary was withdrawn and disposed of immediately before the samples were drawn. The H_2S/H_2 values thus obtained were 10 to 25 pct lower than the values obtained by sampling from the cold zone, the larger deviation being for the lower H_2S contents.

The partial pressure of S_2 in the hot zone is so small that the amount of H_2S formed by cooling will be about 1 pct of the total H_2S. This correction has not been applied in this work. When samples were drawn from the hot zone in a fraction of a second there was some question as to whether the recombination of H_2 and S_2 actually took place.

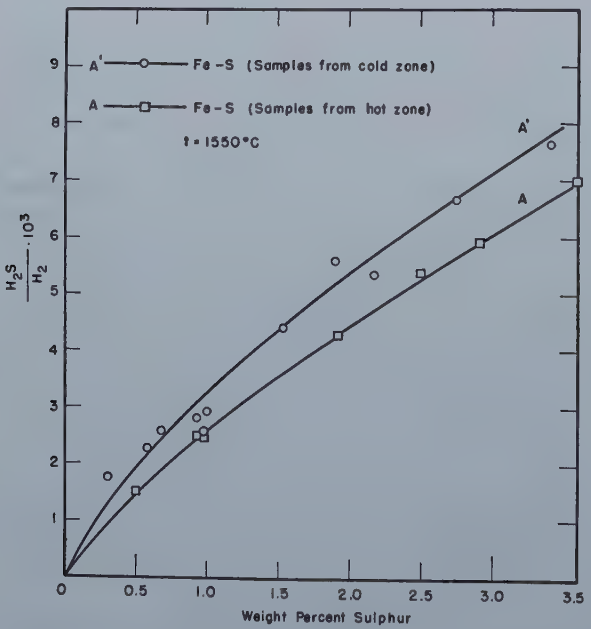

Fig. 2—Variation of H_2S/H_2 with wt pct sulphur for copper-free melts.

Table I. Experimental Runs (1550°C)

Run No.	S, Pct	Cu, Pct	Cu/S(Wt)	$\frac{H_2S}{H_2} \cdot 10^3$
Fe(S) — 63	0.93			2.46
67	0.50			1.50
68	0.98			2.43
69	1.92			4.27
70	2.91			5.91
71	3.60			6.98
72	0.49			1.51
73	0.49	0.64	1.29	1.50
74	0.49	1.95	3.97	1.40
75	1.53	6.04	3.95	2.95
76	2.50			5.42
77	2.43	3.01	1.24	4.39
78	2.28	9.03	3.96	3.72
79	3.40	13.48	3.97	4.66

The H_2S content of the gas was determined iodometrically by means of the same method described in a previous paper;[1] the only difference was that the titration was performed in a hydrochloric acid solution rather than the acetic acid solution. These analyses agreed within a few percent and an average of the three was used.

Each heating period lasted for about 30 hr. During this time the equilibrium value was established for four different compositions.

In a few cases sulphur and copper were determined in the solidified ingot. For this purpose a representative sample (a ¼ sector of the ingot) was cut out, dissolved to completeness in aqua regia, and analyzed gravimetrically.‡ The analytical results agreed satisfactorily with the compositions calculated from the amounts of iron sulphide and copper originally added, corrected for sulphur losses to the atmosphere. Therefore, for all other runs the composition of the melt was calculated and not determined by analysis. The fact that it is possible to keep a material balance of all sulphur and copper

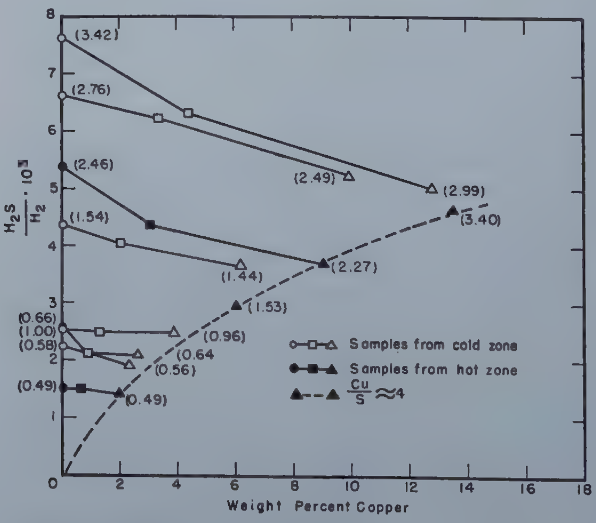

Fig. 3—Variation of H_2S/H_2 as copper is added to the melt.

Figures in parentheses are: to the left, initial sulphur content of the melt; to the right, final sulphur content after dilution with Cu.

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‡ Thanks are due to R. E. Fryxell for the chemical analysis.

added to the steel bath shows that in these runs (all with aluminum oxide crucibles) no significant amount of sulphur was picked up by the refractories. A typical ingot, Fe(S)-71, was analyzed spectrographically and showed the following impurities: Al, 0.002 pct; Si, 0.06 pct; Co, 0.002 pct; Cu, 0.003 pct; and Ni, 0.01 pct.

Experimental Results

The results for those runs where aluminum oxide crucibles were used and samples were drawn from the hot zone are listed in table I. These runs were made at 1550°C.

The Copper-Free Melts: Curve *A* (fig. 2) is based on samples drawn from the hot zone and gives the equilibrium H_2S/H_2 values against weight percent sulphur for pure iron-sulphur melts at 1550°C. Curve *A′* gives the corresponding values for samples from the cold zone. It is apparent that these latter values show a considerably greater scattering than the values in curve *A*. Curve *A* gives for 1 pct S a H_2S/H_2 ratio of $2.55 \cdot 10^{-3}$. The curve has its greatest curvature between 1 and 2 pct S and does not seem to be perfectly linear even below 1 pct S. For very low-sulphur content the ratio $\frac{H_2S}{H_2 \cdot \%S}$ is about $2.8 \cdot 10^{-3}$. These values are slightly higher than those reported by Sherman, Elvander and Chipman.[5]

The Influence of Copper: Copper was added in portions corresponding to weight ratios of copper and sulphur equal to about 1.3 and 4. The latter ratio corresponds closely to the stoichiometric composition (Cu_2S). Fig. 3 shows how the $\frac{H_2S}{H_2}$ ratio in the gas decreases as copper is added to the melt. In this figure are included, for comparison, the data obtained by sampling from the cold zone, and they show the same general trend.

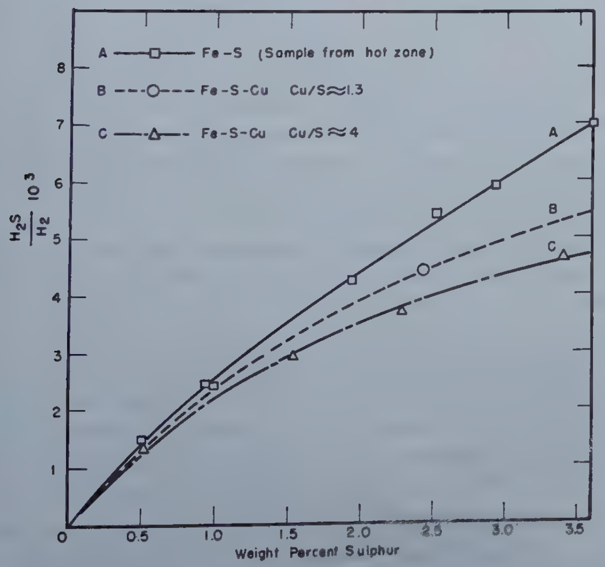

Fig. 4—Variation of H_2S/H_2 with wt pct sulphur for copper-free and copper-containing melts.

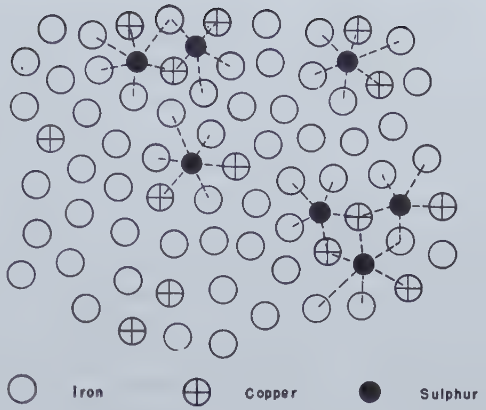

Fig. 5—Two-dimensional sketch of the suggested atomic arrangement for an iron-copper-sulphur melt.

One Fe-Cu-S cluster is indicated at the lower right.

The variation of $\frac{H_2S}{H_2}$ with weight percent sulphur for both copper-free and copper-containing melts is shown in fig. 4. At high-sulphur concentration the sulphur activity is lowered as much as 30 pct when copper is added in amounts corresponding to Cu_2S. At lower sulphur concentrations the effect, absolute as well as relative, becomes less pronounced, and below about 0.5 pct S it is within the limits of experimental error.

It can thus be concluded that the presence of copper alone will not cause any great lowering of the sulphur activity in an iron-sulphur melt with sulphur content of the order of magnitude 0.01 to 0.1 pct. Even if nothing can yet be stated for certain about the effect of copper in a complex steel bath containing elements such as carbon, silicon, and manganese, it is most likely that the effect is too small to hinder the desulphurization process seriously.

The possible effect of copper on the sulphur content of steel is, therefore, limited to reactions at temperatures below melting where metallic copper in scrap may be able to pick up sulphur from the heating gases and form a separate copper sulphide phase, and thus raise the *initial* sulphur content of the steel bath.

Discussion of Results

The effect of copper on the sulphur activity is small but apparent. A traditional explanation would be to say that some of the sulphur in the steel is present as Cu_2S and the remaining as FeS, the relative amounts being determined by the equilibrium:

$$FeS + 2\,Cu \rightleftarrows Fe + Cu_2S$$

A constant for such an equilibrium can be established;[9] but it will have a formal meaning only, and little physical reality, particularly because rather arbitrary assumptions have to be made regarding the relation between chemical activity and concentration of the reactants.

A more satisfactory, although still qualitative, interpretation of the results will be along the lines pointed out by Chipman[10] in his discussion of the oxygen activity in liquid steel and the influence of a third element. Fig. 5 is copied after Chipman's picture of the most likely atomic arrangement in a steel melt where an addition of chromium lowers the activity of dissolved oxygen. The sulphur atoms will be tied by somewhat stronger forces to the copper atoms than to the iron atoms and will be enriched in the neighborhood of the copper atoms. As a consequence of the stronger forces binding it to the melt, the sulphur will have a lower escaping tendency, and therefore a lower activity.

This picture has also another implication. The two binary systems, Fe-Cu and Fe-FeS, show strong positive deviations from ideal mixing. One should expect that copper atoms form short range clusters in the Fe-Cu system and sulphur atoms (most likely as second nearest neighbors) form clusters in the Fe-FeS system, and that the binary melts will have a tendency to separate into two immiscible liquid phases. In the ternary Fe-Cu-S melt, where the sulphur atoms will attract the copper atoms to form as many strong Cu-S bonds as possible, these two types of clusters will unite, and the tendency for separation into two liquid phases will be stronger. This is exactly what happens. The ternary diagram Fe-Cu-S is characterized by an extensive region of liquid immiscibility between a sulphide melt enriched in copper and sulphur, and a "steel" melt enriched in iron.[11] If the sulphur atoms had the greatest affinity for iron, the two types of clusters would have remained separated, and the ternary melts would have no greater tendency for immiscibility than the binary.

Summary

The chemical activity of sulphur in liquid iron has been studied by means of the reaction

$$S(\text{dissolved}) + H_2(g) = H_2S(g)$$

Small amounts of copper were added to the iron-sulphur melts and a decrease in the sulphur activity was observed. This decrease is rather pronounced for large sulphur contents whereas for sulphur contents below 0.5 wt pct S the effect of copper is within limits of experimental error (fig. 4). It is, therefore, concluded that the presence of small amounts of copper will have no significant effect on the sulphur activity in an openhearth steel bath or on the desulphurization process.

A structural model for the iron-copper-sulphur melt is suggested.

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DISCUSSION, C. E. Sims presiding

C. W. Sherman—I would like to compliment the authors on a new approach to the same problem that is being studied at Massachusetts Institute of Technology.

There are several points with which I can concur. We had trouble with contamination of the crucibles due to H_2S being absorbed in the alumina. However, when we went to a very pure alumina that had been specially purified, we got a very low pickup on the crucibles. The effect of silicon contamination had been studied by Morris and Williams and a correction should be applied whenever possible.

I think it is a little bit too early to conjecture about the construction of the melts. In a thermodynamic study, I think it is better to collect the thermodynamic data and not worry too much about whether the copper likes the sulphur better than the iron likes the sulphur.

R. C. Buehl—I merely wanted to say that we had tried the effect of adding copper and also found that it lowered the activity coefficient of sulphur to a very small extent, similar to what was found in this investigation.

T. Rosenqvist (authors' reply)—As far as the purity of the refractories and possibility for sulphur pickup are concerned, the crucibles, as well as the chimney tube we used, were of high purity from Norton Co. They contained more than 99 pct aluminum oxide, the rest being mostly sodium. No silica was reported, and no significant sulphur pickup could be detected. The silicon in the metal was most probably due to silica in the mullite tube which was reduced and transferred through the vapor to the melt.

The presence of silicon to the order of 0.05 pct will, according to the work by Morris and Williams, increase the sulphur activity by about 1 pct. This I regard as insignificant.

The atomic arrangement that I suggested is sketchy and preliminary. I think there has been too much talk in the other direction, such as discussions whether the sulphur is present as iron sulphide or copper sulphide. I merely wanted to suggest another alternative.

C. W. SHERMAN, formerly Massachusetts Institute of Technology, Cambridge, Mass., now Latrobe Electric Steel Corp., Latrobe, Pa.; R. C. BUEHL, U. S. Bureau of Mines, Pittsburgh, Pa.

Graphite-Rod Hairpin-Resistor Radiation Furnace For High Temperatures

by W. J. Kroll, W. W. Stephens, and J. P. Walsted

FOR the production of carbides, various furnace types are available, especially those using arc, resistance, and high-frequency heating. Selection of a specific means of heating depends primarily on the material to be treated and the physical properties of the carbide produced. In the present case, zirconium carbide had to be prepared on an industrial scale as a raw material for the production of anhydrous zirconium chloride. Considering that a rather expensive pure oxide was to be used, the arc-furnace treatment recommended for zircon sands in a previous publication[1] was ruled out because of the considerable volatilization and dust losses caused by the blast of the arc. For this reason, either high-frequency or resistance heating seemed to offer more promise. Since there was not enough capacity of the former available, resistance heating was chosen.

It was first thought that the Acheson silicon carbide furnace would be suitable for the present purpose, but the voltage in such a furnace, in which the current passes through the batch, varies from 220 to 75 v from the start to the end of a run. This variation is so great that a special tap transformer would have been required. Trouble was also expected by local melting of the carbide. Pure zirconium carbide melts at about 3527°C, but the melting point is brought down to 2427°C, according to Agte,[2] when an excess of 6 pct C is present in the carbide. This we found confirmed by experiments in a high-frequency furnace. Excess carbon is needed in the batch to obtain a complete reduction. Fusion of the charge would cause great difficulties in an Acheson-type furnace because of the good electrical conductivity of the carbide as compared with that of the loose batch. Also, fused carbide is much more difficult to chlorinate than the spongy product that can be made in the radiation furnace described below. It was apparent that, to obtain a good-quality zirconium carbide, the heat input would have to be well-controlled. The hairpin-resistor principle seemed to offer possibilities in this regard, and a furnace of this type was therefore developed.

The advantages of the hairpin-resistor radiation principle have been discussed in previous publications, and a split-tube graphite-resistor furnace,[3] now increasingly used in various laboratories, as well as a centrifugal quartz melting furnace[4] of this type, has demonstrated the usefulness of this heating method.

The hairpin-heater element has the following definite advantages over a straight resistor of the type used, for instance, by Georges:[5] Its resistance is four times greater; it can expand freely; it is sturdier because of the larger diameter, and it has a larger radiation surface; there are no hot contacts that might wear out or overheat; only one clamp is used which permits assembling all electrical leads at one side of the furnace, making the other sides easily accessible to the operator. The shorter element and its larger diameter permit greater concentration of heat.

The furnace developed is shown in fig. 1. The box (*1*), made of 2½-in. graphite plates, has inside dimensions of 23x17x16 in. It contains the briquetted batch (*2*). The box is embedded in lampblack (*3*) up to the cover plate. The cover plate contains an opening for the gas escape (*4*) and for the observation hole (*5*), which permits measuring the temperature with an optical pyrometer. The cover plate is embedded in charcoal (*6*). The lampblack is contained in the insulating brick lining (*7*), held in the ¼-in. sheet steel box (*8*). The graphite box is set on two rows of triangular graphite bars (*9*). The hairpin-heater element (*10*), the dimensions of which are given below the main drawing, extends horizontally in the graphite chamber and radiates freely on the batch. A graphite tube (*11*) keeps the lampblack from falling into the slot. The split electrode, which in reality is turned 90° against the drawing, is so arranged that the slot is vertical. The water-cooled packing gland (*12*) is insulated by an airgap from the heater element. A thin pipe (*13*)

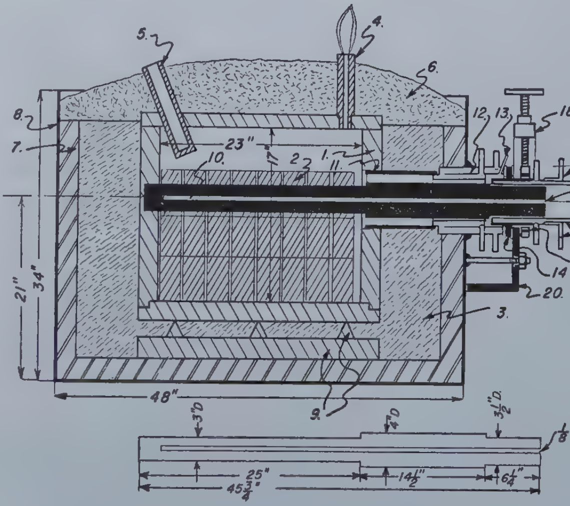

Fig. 1—Zirconium carbide furnace.

1. Graphite box
2. Batch
3. Lampblack insulation
4. Gas escape pipe of graphite
5. Observation hole
6. Charcoal cover
7. Insulating brick lining
8. Steel plate shell
9. Triangular supports of graphite
10. Hairpin-heater element of graphite
11. Graphite tube
12. Water-cooled gland
13. Nitrogen inlet
14. Clamp flange with rubber gaskets
15. Asbestos sheet insulator
16. Water-cooled electrode clamp
17. Bus bars
18. C clamp
19. Transite plugs
20. Adjustable L-holder

W. J. KROLL, Member AIME, is Consulting Metallurgist, W. W. STEPHENS, Junior Member AIME, and J. P. WALSTED are Metallurgists, Northwest Electrodevelopment Laboratory, U. S. Bureau of Mines, Albany, Oregon.

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AIME St. Louis Meeting, February 1951.

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permits introduction of nitrogen in this gap. Two rubber gaskets make the joint between the flange (*14*) of the split clamp and the gland. The slot contains an insulating sheet of asbestos board (*15*) within the clamp. The water-cooled electrode clamp (*16*) is connected with flexible cables to the transformer by way of the bus bars (*17*). A C clamp (*18*) pinches the two halves of the electrode clamp together to make good contact with the electrode and is insulated from this clamp by transite spacers (*19*). The flange of the electrode clamp is pressed tightly against the gland with the adjustable holders (*20*). Loose asbestos is packed in the slot between electrode clamp halves to make a tight joint.

The results obtained with this furnace will be described with one typical example. A batch of 234 lb was made up of 170.3 lb of pure zirconium oxide, 46.7 lb of lampblack, and 7 lb of dextrine. The oxide and carbon were intimately mixed in a concrete mixer, and dextrine was added as water solution. The damp mixture was briquetted in a 50-ton briquet press, making two 9x4½-in. bricks in one stroke. The specific pressure was only about 1230 psi. The bricks were dried in a core oven at 250°F (120°C). They were deposited in the graphite container of the carbide furnace with some spacing between each two to permit free escape of gas. The upper layer was so arranged as to leave a channel for the split heater electrode. A direct contact of the batch with the resistor must be avoided.

The temperature, voltage, and power input of this run are plotted against time in the diagram, fig. 2. The voltage varies only between 28 and 23 v. It can be seen that the temperature of 1657°C, at which the CO pressure of the carbon-zirconium oxide mixture reaches 1 atm, according to Prescott,[6] is obtained after about 2 hr. Lorenz gives slightly higher reaction temperatures.[7] Kieffer[8] reduces at 1700° to 1800°C. Rapid gas evolution is observed at 1800°C. After holding for 11 hr at or above this limit, the temperature tends to rise because most of the reaction, which consumes power, is over. At this moment the power input is reduced by tap change, and the batch is held to 1900° to 2000°C for 4½ hr. The total time of this run was 19½ hr. It took 2 days to cool the furnace to room temperature, which makes one cycle last about 3 days. Artificial cooling might be applied.

The power consumption, measured at the meter, was 920 kw-hr. Since the output of carbide was 161 lb, the power consumption amounted to 5.72 kw-hr per lb of carbide produced. The weight loss of 73 lb observed for the 234-lb batch represents, according to a calculation, a conversion of oxide to carbide of better than 99 pct. The average zirconium content of 7200 lb of carbide made in various runs was 78.15 pct. A metal balance made after processing 4200 lb of oxide showed a loss of only 2.1 lb, which is negligible.

The carbide made in the radiation furnace is a porous, gray-black mass, with inclusions of excess carbon. It is friable and disintegrates in the chlorination. This carbide was found to chlorinate much better than the dense product made by fusion in the arc furnace.

The radiation furnace is a good tool for producing various high-melting carbides, but its limitations must be stressed. When used for reducing readily reducible ores or oxides in which carbon dioxide is formed, the resistor is burned up at a rapid rate. Even with zirconium oxide, it appears that the resistor is consumed by carbon dioxide, which may form in the early phase of the reduction. Another cause for the attack of the electrode is the presence of moisture in the batch. With zirconium oxide as raw material, one electrode lasts three runs, which represents a graphite consumption of about 0.065 lb per lb of carbide produced. It would not be advisable to reduce zircon sands in the radiation furnace, since the product obtained initially in this reduction is zirconium silicide, which fuses at about 1350°C and would liquate to the bottom of the graphite box, where it would cause heavy corrosion of the graphite plates.

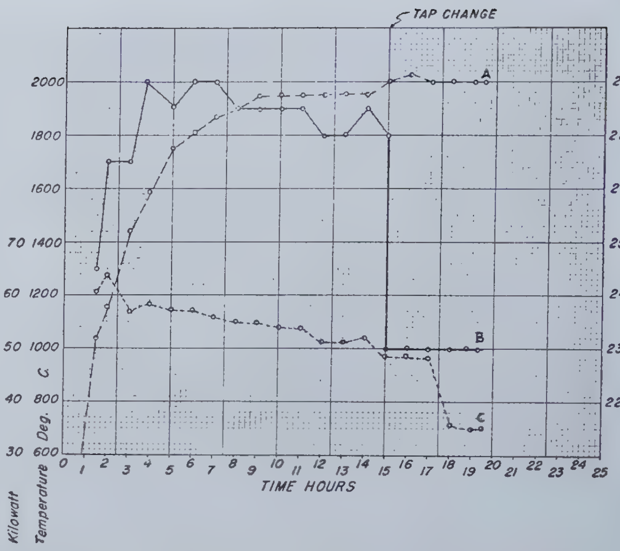

Fig. 2—Performance data of zirconium carbide furnace.

Temperature, voltage, and power input in function of time. *A*—Temperature. *B*—Voltage. *C*—Power input.

Conclusion

The hairpin graphite-resistor radiation furnace is well-adapted for producing zirconium carbide from oxide at temperatures between 1800° and 2000°C with 100 pct recovery of the zirconium content. The power consumption in a rather small furnace is only about 5.7 kw-hr per lb of carbide produced. The voltage variation during the run is slight, so that cheap transformers can be used to supply the energy. The carbide obtained is of very good quality as far as its amenability to chlorination is concerned. The furnace described may be well-adapted for producing other high-melting carbides or borides, such as titanium carbide or boride. It cannot be recommended for reducing oxides that develop large quantities of CO_2, since this gas consumes the electrode at a rapid rate.

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Production of Titanium from $TiCl_4$ in an Arc Furnace

by L. D. Jaffe and R. K. Pitler

It would clearly be advantageous to produce molten titanium, suitable for alloying and casting, directly from the relatively inexpensive tetrachloride, without using a metallic reducing agent. Accordingly, a preliminary investigation has been made of the production of titanium by hydrogen reduction of the tetrachloride in an electric arc furnace.

For the reaction:

$$TiCl_4(g) + 2H_2(g) \rightarrow Ti(s) + 4HCl(g),$$

Lockhart and his colleagues[1] have calculated equilibrium constants at 800° to 1500°K, based on tables of Brewer.[2] Extrapolating these data on the assumption that the heat of reaction varies linearly with temperature, and using Brewer's value for the heat of fusion, there is obtained for the reaction:

$$TiCl_4(g) + 2H_2(g) \rightarrow Ti(l) + 4HCl(g)$$

an equilibrium constant at 2100°K (100° above the melting point)

$$K_p = (p_{HCl})^4/p_{TiCl_4}(p_{H_2})^2 = 0.167 \text{ atm.}$$

If this is correct, starting with hydrogen saturated with $TiCl_4$ at 25°C, where the vapor pressure of the latter[3] is 12.6 mm, and maintaining the overall pressure at 1 atm, 99¼ pct of the $TiCl_4$ would be reduced to Ti at equilibrium.

An arc furnace designed for the melting of titanium and lined with water-cooled copper was used for the preliminary experimental check. Its inside diameter was 2 7/16 in. and height 6 in. The water-cooled electrode was tipped with ¾ in. diam tungsten. In the one run carried out, the furnace was charged with a starting batch of 293.35 g of scrap titanium,[4] analyzing 99.24 pct Ti. After the system was twice pumped out and flushed with argon to remove air, the arc was struck in argon and kept at 400 amp dc, electrode negative, for 1 min to melt the starting batch. Commercial tank hydrogen, dried by passing over silica gel and bubbled through technical grade $TiCl_4$ at room temperature, was then admitted to the furnace. The inlet tube directed this gas downward toward the arc and melt; the gas outlet was at the top of the furnace. The quantity of gas passed through was not measured accurately but is estimated to be about 50 liters per min at a few mm of mercury above atmospheric pressure.

The arc was held in the H_2-$TiCl_4$ mixture at 400 amp with little difficulty. After 10 min the arc burned through the copper lining above the melt, admitting water and ending the run. (This had happened frequently in straight melting runs under argon, and is not thought due to the atmosphere used.) In the furnace were found an ingot, several small pieces, and a little metallic powder, evidently formed when water entered the hot furnace. Some titanium also clung to the electrode. The portions were weighed and separately analyzed for titanium. Their total weight was 321.76 g of 94.82 pct overall purity. Much of the impurity consisted of tungsten broken off when the titanium was removed from the electrode. No detailed impurity analysis was made because the starting materials were impure and flooding the furnace introduced further contamination.

Thus, the metal recovered contained 305.08 g Ti, as compared to 291.12 g in the starting batch. Titanium could not have been carried over from previous melting runs in the furnace, as the interior was sandblasted and the electrode ground clean before the run. Evidently at least 13.96 g of Ti were produced from $TiCl_4$. Since this would require complete reduction of 430 liters of $TiCl_4$ gas at 12.6 mm of Hg, the efficiency of the process must have been rather high.

Experimental work is continuing. No reason is seen why the process could not be scaled up to the size of a 30-ton steel-melting arc furnace. In a large unit there would be a large molten pool from which liquid metal could be withdrawn for alloying and casting. The problems of electrodes and power supply are similar to those arising in arc furnaces for melting titanium. Unreacted $TiCl_4$ and the HCl in the exhaust gases could be recovered; unreacted H_2 could be dried and re-used.

The melt would be saturated with hydrogen, whose solubility in liquid titanium is unknown. Small amounts of hydrogen seem to have little effect on the properties of titanium.[5] If the amount introduced was so large as to impair properties or cause casting difficulties, it could be reduced by holding the melt under an inert gas or by pumping on it, prior to casting.

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TN 49 D. Manuscript received Sept. 11, 1950.

Acknowledgment

The authors would like to thank I. Preble and M. Goldman for their valuable aid in the experimental work and the thermodynamic calculations, respectively.

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aime NEWS

Dues Statements In Mail; Publication Prices Remain Unchanged

To lighten the year-end peak load at AIME headquarters and assure prompt mailing of 1951 membership cards, statements of 1951 dues are being mailed to AIME members by groups in the closing months of 1950. Despite increased printing costs, no change is being made in the subscription prices of the Journals or Transactions volumes for the coming year. Each paid-up Institute Member (except Student Associates paying $2) will receive an annual subscription to a Journal of his choice without further charge. Nonmember subscriptions are $8 domestic and in the Americas and $9 elsewhere. To comply with postal requirements $6 of the annual membership fee is credited as a subscription to a Journal, ($4 for Student Associates). If a member wishes to receive a second Journal, he may be put on the subscription list by payment of an additional $4, or for $8 additional he may receive all three Journals. However, if two or more copies of the **same** Journal are desired, the nonmember rates apply for the additional subscriptions.

Transactions volumes, which are reprints of the Transactions sections of the monthly Journals, are $3.50 each when payment is made for them in advance of publication along with dues. Otherwise, the member is billed at the regular price of $7, less a 30 pct member discount. As was done last year, three Transactions volumes will be issued early in 1951, covering all the material that appeared in 1950, one each for the Mining, Metals, and Petroleum Branches.

This year the material contained in the former annual Petroleum Statistics volumes is being printed from month to month in the Journal of Petroleum Technology, but can be obtained in a bound volume for $3 to members or $6 to nonmembers. It should be available early in 1951, as soon as publication of the statistics in the monthly Journals has been completed.

Service Inductees Put on Inactive List

Because of requests from men currently being inducted into military service that their memberships in AIME be put on an inactive status, a procedure was authorized by the Executive and Finance Committees at their meeting on Aug. 16, 1950.

Upon individual request from Members and Student Associates entering military service in the present emergency, the Secretary is directed to offer temporary suspension of their AIME membership until such time as they may reenter professional work. No membership fees will be charged and none of the usual privileges of membership will be extended, but the Member's original election date will be preserved, and he will be entitled to any credits that may be authorized on initiation fees for continuous dues-paying membership. Each such request will be handled on an individual basis, the action taken by the Secretary to be reported to the Executive Committee for approval. The Secretary will maintain a cumulative list of all members granted such suspension.

Agricola's "De Re Metallica" Reprinted

A reprint of the Hoover translation of Agricola's "De Re Metallica" is soon to be available. The original volume long has been a collector's item, and has sold at several times its publication price. The new edition will be printed by offset from plates made from the first edition, will be of substantially the same size, and attractively bound. The list price will be $10. A total of 1400 copies have been purchased by the Seeley W. Mudd Fund of the AIME for distribution to new Junior Members of the Institute through the courtesy of the Fund.

Changes of Address

When notifying AIME headquarters of a change of address, or of company position or affiliation, please mention the Branch of the Institute to which you belong—Mining, Metals, or Petroleum. This will make for a more expeditious handling of the change and will facilitate the preparation of various reports.

Metals and All-Institute Divisions Officers Appointed

Officers have been named for the three divisions of the Metals Branch of AIME for the coming year, as well as for the Mineral Economics and the Mineral Industry Education Divisions.

Institute of Metals Division: R. M. Brick, chairman; W. A. Dean, senior vice-chairman; J. H. Scaff, vice-chairman; E. O. Kirkendall, secretary; and an executive committee to serve for three years composed of J. B. Austin, W. R. Hibbard, Jr., and C. H. Samans.

Extractive Metallurgy Division: O. C. Ralston, chairman; T. D. Jones, chairman-elect; E. O. Kirkendall, secretary; and an executive committee to serve from 1951 to 1954 composed of L. P. Davidson and R. D. Bradford.

Iron and Steel Division: T. L. Joseph, chairman; and W. C. Kitto, J. B. Austin, and E. K. Miller, vice-chairmen. An executive committee to serve for three years was appointed, consisting of R. W. Campbell, J. A. Bowers, and F. L. Toy.

Minerals Economics Division: R. J. Lund, chairman; and G. S. Borden, J. W. Feiss, R. P. Koenig, vice-chairmen. Secretary-treasurer is John H. Melvin; and the executive committee is composed of Evan Just, R. H. Bennett, and G. W. Josephson.

Minerals Industry Education Division: Allison Butts, chairman, H. H. Power, vice-chairman; C. L. Wilson, past-chairman; and an executive committee to serve from 1951 to 1953, G. B. Clark, R. M. Brick, and E. H. Wisser.

Technical and Auxiliary Publications Committees Named

The Technical and Auxiliary Publications Committees for the coming year were appointed at the Sept. 20, 1950, meeting of the Executive and Financial Committees. These committees consist of:

Technical Publications Committee — Francis B. Foley, chairman; J. I. Laudermilk, vice-chairman; C. H. Lambur, vice-chairman; E. J. Kennedy, Jr., secretary; and M. D. Hassialis, R. H. Aborn, C. H. Behre, Jr., P. B. Bucky, V. H. Clarke, C. W. Eichrodt, P. F. Kerr, W. H. Loerpabel, E. W. Palmer, L. C. Raymond, J. S. Smart, Jr., and Felix E. Wormser. Members ex-officio include E. O. Kirkendall, E. J. Kennedy, Jr., and E. H. Robie. Acceptances to serve on this committee have been received from all but three appointees.

Auxiliary Publications Committee

Extractive Metallurgy Division: P. T. Stroup, chairman, and M. A. Hunter and J. D. Sullivan. Two additional members to this committee will be appointed. *Iron and Steel Division:* F. M. Washburn, chairman, and A. G. Forrest, B. R. Queneau, T. F. Plimpton, M. Tenenbaum, and Otto Zmeskal. A committee for the Institute of Metals Division has been tentatively chosen, awaiting Board approval and acceptance from the members.

C. E. Weed To Get Saunders Medal

Clyde Evarts Weed, vice-president in charge of mining operations, Anaconda Copper Mining Co., has been selected to receive the William Lawrence Saunders Medal for 1951. It recognizes distinguished achievement in mining. It will be presented to Mr. Weed at the Annual Banquet of the AIME in St. Louis, Feb. 21, 1951. The recommendation was made to the AIME Board of Directors by a committee of which William J. Coulter was chairman. The citation reads as follows:

> "Having brought to the metal mining industry a new concept of technological and operating efficiency, thus saving for the industry and for the world badly needed and valuable resources; also, for having envisioned and brought to fruition a development and exploration program, along modern and scientific lines, that is proving very helpful in the perpetuation of the industry."

Hoover Medal Winner Named

Dr. Karl T. Compton, of Massachusetts Institute of Technology, Cambridge, Mass., has been elected the 12th recipient of the Hoover Medal (1950). It will probably be conferred upon him during the winter meeting of the American Institute of Electrical Engineers next January.

Dr. A. Nadai Completes Monograph

The latest addition to the Engineering Societies Monographs Series is the *Theory of Flow and Fracture of Solids* by A. Nadai, the first of a two-volume revision and expansion of Dr. Nadai's *Plasticity,* which was the first volume published as a Monograph when the series started in 1931. The Monographs are selected by a committee composed of members of ASCE, AIME, ASME, and AIEE, with Reed W. Hyde and E. M. Wise representing AIME at the present time. McGraw-Hill Book Co. Inc. are the publishers of the series by arrangement with Engineering Societies.

New Local Section To Form In Mexico

At its meeting on Sept. 20, the Executive and Finance Committees of the AIME approved a petition from a group of members in Mexico to form a new Local Section with headquarters in Mexico City. The petitioners were: Alfredo Terranzas, Jenaro Gonzales R., Eduardo Mapes V., Eugenio Tavera A., G. A. Joslin, Hugh Rose, J. R. Woodul, A. Terrones Benitez, V. R. Garfias, Jose A. Garcia, Victor Cerate, M. F. Tynan, A. W. Edelen, Wm. G. Kane, and J. G. Reilly. The name of the new Section, its officers, bylaws, and area to be embraced remain to be decided. One of the first activities of the new Section will be to plan for the Fall Meeting of the Institute, to be held next year in Mexico City. The prospective dates are now Oct. 29 to Nov. 3, subject to approval of the local groups.

"Coal Preparation" In Revised Edition

The second, completely revised edition of "Coal Preparation" was published in October, and is now available for $8, less 30% discount to AIME members and Student Associates, and to public libraries, and 20% discount to booksellers. The first edition was published in 1943 and has recently been out of print. The revision, like the original edition, has been edited by David R. Mitchell. All the latest practices developed in the last seven years are covered in this 830-page volume. It is not only of great value to operating men but is being used as a text and reference book at many colleges. Publication was again under the sponsorship of the Seeley W. Mudd Memorial Fund Committee.

AIME Student Chapter Recognition

A new policy as to the recognition of AIME Student Chapters was voted by the Board of Directors at their meeting on Aug. 29. Because of the fact that the activity of many of them has been intermittent, they will hereafter be recognized for only a year at a time, such recognition being subject each year to the approval of the Local Section in whose territory the Student Chapter lies. The Local Section will also assist the Chapter in every way it can, and will seek to reactivate a Chapter that has become inactive if it feels that good can be accomplished thereby. A folder containing material useful to Local Sections in their contact with Student Chapters has recently been prepared and is available from Institute headquarters.

C. W. McCoy Wins Student Award

Clifford W. McCoy, a junior in metallurgical engineering at Carnegie Institute of Technology, has been awarded the Lewis E. Young award for the year 1950-51.

The Award is given by the Women's Auxiliary of the American Institute for Mining and Metallurgical Engineers, and is presented in honor of Dr. Lewis E. Young, past president of the Institute.

The award, given on the basis of character and high scholastic achievement, is made to a Carnegie student every third year, with similar awards at Penn State and the University of Pittsburgh in the intervening years.

A. B. Kinzel To Deliver Howe Lecture

A. B. Kinzel has been named to deliver the Howe Memorial Lecture at the Annual Meeting of the AIME in New York in 1952. The name of the lecturer is recommended by the Iron and Steel Div., Metals Branch, of the Institute. Dr. Kinzel is president of the Union Carbide and Carbon Research Laboratories, New York.

Proposed for Membership—Metals Branch AIME

Total AIME membership on Sept. 30, 1950, *was* 16,737; *in addition* 4,184 *Student Associates were enrolled.*

ADMISSIONS COMMITTEE

E. C. Meagher, Chairman; Albert J. Phillips, Vice-Chairman; George B. Corless, H. P. Croft, Lloyd C. Gibson, Ivan A. Given, F. W. Hanson, T. D. Jones, P. Malozemoff, Richard D. Mollison, and John Sherman.

Institute members are urged to review this list as soon as the issue is received and immediately to wire the Secretary's office, night message collect, if objection is offered to the admission of any applicant. Details of the objection should follow by mail. The Institute desires to extend its privileges to every person to whom it can be of service but does not desire to admit persons unless they are qualified.

In the following list C/S means change of status; R, reinstatement; M, Member; J, Junior Member; AM, Associate Member; S, Student Associate.

Alabama

Florence—Jordan, Robert E. (J)

Connecticut

East Hartford—Paquette, Donald G. (J) (R. C/S—S-J).

Illinois

Aurora—Weston, Perry L. R. Jr. (J) (C/S—S-J).

Chicago—Campbell, Cyril J. (M). Gray, Robert A. (A). Ikeuye, Kay K. (J) (C/S—S-J). La Pota, John B. (M). Nelson, Francis D (J) (C/S—S-J). Sheehan, John P. (M) (R. C/S—S-M).

Gurnee—Pantell, James W. (J).

Homewood—Caskey, George R. Jr. (J) (C/S—S-J).

Zion—Cotton, Hiram E. Jr. (J) (C/S—S-J)

Indiana

Hammond—Lambert, William N. (J).

Kentucky

Anchorage—Perkins, George (M).

Massachusetts

Boston—Tomlinson, John W. (J).

Cambridge—Funk, Edward R. (J) (C/S—S-J)

Greenwood—Almeida, A. R. (J).

Malden—Steck, Alfred B. (J) (C/S—S-J)

Michigan

Niles—Kenny, James B. (M).

Minnesota

Minneapolis—Lund, Louis M. Jr. (J) (C/S—S-J)

Missouri

Independence—Grayer, George D. (M) (R. C/S—S-M).

Mexico—Schroeder, Frederic, W. (M) (R. M).

New Jersey

Ridgewood—Bittmann, Charles A. (J) (C/S—S-J)

New York

Arverne—Peckner, Donald M. S. (J) (C/S—S-J).

Buffalo—Gietzen, Eugene A. (M).

Lockport—Ross, Stuart T. (J) (C/S—S-J)

Rome—Poland, Frank F. (M).

Ohio

Cleveland—Garibotti, Domenick J. (J) (C/S—S-J). Minto, Robert E. (M).

Cleveland Heights—Lanner, Hans S. (J.) (C/S—S-J).

Columbus—Davis, Howard F. (J) (C/S—S-J).

Pennsylvania

Kingston—Brown, Thomas E. (M).

Murraysville—Wright, Emerson H. (J) (C/S—S-J).

Pittsburgh—Dobin, Harry (M). Lambert, Robert A. (M). McConnon, Thomas C. (J) (C/S—S-J). Pound, Guy M. (J). Weinbaum, Morris J. (J) (C/S—S-J). Wiener, George W. (M).

Scottdale—Barclay, Frank H. (M).

State College—Wilde, Howard DeF. (J) (C/S—S-J).

Utah

Magna—Dean, Robert L. (J).

Salt Lake City—Soupcoff, Thomas N. (J).

Virginia

Richmond—Schmidt, Walter (M).

West Virginia

Huntington—Edwards, Paul H. (M).

Canada

Trail, B. C.—Weldon, Thomas H. (M).

Egypt

Abbassia, Cairo—Nassim, Ramses L. (J) (C/S—S-J).

England

Kent—Phillips, Victor A. (J) (C/S—S-J).

Japan

Tokyo—Tokunaga, Sunao (M).